

MOLECULAR RESPONSE FROM A SEMIEMPIRICAL WAVEFUNCTION

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PREFACE

"What a long, strange trip it's been."

(Truckin', Bob Weir & Jerry Garcia, 1971.)

TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGEMENTS	ii
PREFACE	iii
ABSTRACT	vi
BACKGROUND	1
The Schrödinger Equation	1
The Representation of the Electronic Wavefunction	5
The Hartree-Fock Equations	8
The Intermediate Neglect of Differential Overlap	13
INTRODUCTION	19
Rayleigh-Schrödinger Perturbation Theory	19
The Propagator	25
The TDA Representation of States	30
The RPA Representation of States	34
The Representation of States for the Propagator	37
DETAIL	43
The TDA Expression of RSPT	44
The RPA Representation for the Propagator	52
The Matrix Inverse Algorithm	54
Integral Processing	59

APPLICATION: ELECTRIC FIELD RESPONSE	62
Electric Field Properties	62
Polarizability	65
Hyperpolarizability	69
Dynamic Molecular Polarizability	74
APPLICATION: NUCLEAR SPIN-SPIN COUPLING	82
Theory of Nuclear Spin-Spin Coupling	82
Survey of Sum-Over-States Approaches to Coupling	89
The Finite Field Method	91
Proton Couplings	94
Couplings Including the Dipolar and Orbital Terms	100
CONCLUSION	102
REFERENCES	108
BIOGRAPHICAL SKETCH	118

Abstract of Dissertation Presented to the Graduate School
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MOLECULAR RESPONSE FROM A SEMIEMPIRICAL WAVEFUNCTION

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The subject of this dissertation is the determination of molecular response properties from a semiempirical electronic wavefunction. The wavefunction is calculated from an energy functional, and describes the degrees of freedom for the electrons which constitute a given molecular system. By the term semiempirical, it is inferred that experimental data is incorporated in the procedure for determination of the wavefunction. The specific semiempirical method of interest will be the Intermediate Neglect of Differential Overlap (INDO) model Hamiltonian. Molecular response is related to the moments of expansion of the power series expression for the energy of a molecule in the presence of an external perturbing influence.

Through Rayleigh-Schrödinger Perturbation Theory (RSPT), expressions are developed for the second- and third-order static-field energy expressions. The Tamm-Dancoff Approximation (TDA) and the Random Phase Approximation (RPA) are introduced as representations of the states which comprise the RSPT procedure. Green's function techniques and the theory of propagators are presented to describe the response of a system under the influence of a time-varying perturbation. The RPA method is shown to be

consistent with the moment expansion of the propagator. Using the inversion of the TDA and RPA energy representations, an efficient algorithm is developed to perform the calculation of the energy expressions. A method of integral processing is employed which allows the algorithm to be accomplished in an amount of time on the same order of magnitude as the construction of the wavefunction.

The methods are applied to the calculation of INDO/S static molecular polarizability and hyperpolarizability, and dynamic polarizability. The effects of basis set are discussed. The technique is then applied to the determination of nuclear spin-spin coupling constants.

BACKGROUND

The emphasis of this chapter is on the fundamental aspects of molecular electronic structure theory, and the development of a systematic approach to obtain numeric results from the basic formalism. The first section begins by reviewing *a priori* the assumptions necessary for the solution of the quantum mechanical equations describing a collection of interacting particles. The statistics of the electron are discussed as being consistent with a determinantal representation of the electronic wavefunction. Second quantization is introduced as an algebraically equivalent construct for the electronic degrees of freedom. The Hartree-Fock (HF) Self-Consistent Field (SCF) method is developed as a means to approximate the exact N-particle wavefunction as an antisymmetrized product of N one-particle functions or orbitals. The approximations used in the valence-only Zero Differential Overlap HF methods are then discussed.

Throughout this paper, the use of atomic units ($\hbar, e, m_e, 4\pi\epsilon_0 = 1$) is implicit, as well as the convention of indices i,j,k,.. for occupied (or hole) states, a,b,c,.. for unoccupied (or virtual or particle) orbitals, and p,q,r,.. for an unspecified orbital.

The Schrödinger Equation

A basic premise of the quantum mechanics of an interacting system is the existence of the wavefunction which, in the Schrödinger formulation¹⁻⁴, may be represented as $\Psi(\xi, t)$. In the Schrödinger picture, the wavefunction is dependent on time (t) and contains variables relating to the individual degrees of freedom (ξ) of its constituent particles.

To give physical meaning to $\Psi(\xi, t)$, the Born interpretation postulates that the probability density of finding a particle in the region of space $d\tau$ is given by $|\Psi(\xi, t)|^2$. A physical property which is characterized by the operator $\hat{A}$ may be measured as an expectation value by summing its action on the probability density over all infinitesimal volume elements

$$\int \hat{A} |\Psi|^2 d\tau = \int \hat{A} \Psi \Psi^* d\tau = \int \Psi^* \hat{A} \Psi d\tau = \langle \Psi | \hat{A} | \Psi \rangle . \quad (1.1)$$

The Dirac bra-ket convention is introduced on the right-hand side of Eq (1.1), in which all components of the “bra”—or operators acting on these functions—are complex conjugated

$$\begin{aligned} \hat{A} | \Psi \rangle &= \hat{A} \Psi \\ \langle \Psi | \hat{A} &= (\hat{A} \Psi)^* . \end{aligned} \quad (1.2)$$

Integration is implied when a “bra” or “ket” function is multiplied by its conjugate function.

The quantum mechanical operators which provide a means to measure the physical properties of a system will be assumed to behave linearly

$$\hat{A} (\lambda \Psi_1 + \mu \Psi_2) = \lambda \hat{A} \Psi_1 + \mu \hat{A} \Psi_2 \quad (1.3)$$

and those corresponding to real observables must necessarily be Hermitian

$$\int (\hat{A} \Psi_1)^* \Psi_2 d\tau = \int \Psi_1^* \hat{A} \Psi_2 d\tau . \quad (1.4)$$

The time-evolution of the quantum mechanical system is governed by the time-dependent Schrödinger Equation

$$i \frac{\partial \Psi(\xi, t)}{\partial t} = \hat{T} \Psi(\xi, t) + \hat{V}(\xi, t) \Psi(\xi, t) . \quad (1.5)$$

In Eq (1.5), $\hat{T}$ represents the kinetic energy operator for the particles, and $\hat{V}$ their potential for interaction. If for the moment $\hat{V}$ is assumed time-independent, the variables of Eq (1.5) may be separated, and the wavefunction written in the product form

$$\Psi(\xi, t) = e^{-iEt} \bar{\psi}(\xi) . \quad (1.6)$$

The function $\bar{\psi}(\xi)$ solves the time-independent Schrödinger Equation

$$\hat{T} \bar{\psi}(\xi) + \hat{V}(\xi) \bar{\psi}(\xi) = E \bar{\psi}(\xi) . \quad (1.7)$$

For a wavefunction expressed in the form of Eq (1.6), assuming the value E to be real, the probability density is time invariant

$$|\Psi(\xi, t)|^2 = |\bar{\psi}(\xi)|^2 . \quad (1.8)$$

In this case, the function $\bar{\psi}(\xi)$ completely characterizes the “stationary state” probability density $|\Psi(\xi, t)|^2$. The term stationary state is not in regard to the electronic motions, but with respect to the probability density. Expectation values for any time-independent operator may then be measured from the stationary state probability density, according to Eq (1.1). The subsequent discussion, unless explicitly noted, will deal with the time-independent Schrödinger Equation and the wavefunction will be the stationary-state form $\bar{\psi}(\xi)$.

The focus now is to treat the quantum mechanical stationary state system of electrons and nuclei comprising a molecule. As a first approximation, the solution for the time-independent Schrödinger Equation is assumed to be in the non-relativistic form, implying that the electronic motions are slow relative to the speed of light, and interactions involving the intrinsic angular momentum of the electron— spin-orbit and spin-spin

coupling— are neglected. This Hamiltonian is then

$$H = \hat{T} + \hat{V} = -\frac{1}{2} \sum_i \nabla_i^2 - \frac{1}{2} \sum_A \frac{\nabla_A^2}{m_A} - \sum_{i,A} \frac{Z_A}{r_{iA}} + \sum_{i<j} \frac{1}{r_{ij}} + \sum_{A<B} \frac{Z_A Z_B}{r_{AB}} \quad (1.9)$$

with the sum $i, j, \dots$ over electrons and $A, B, \dots$ over nuclei. The first two terms comprise the kinetic energy operator T for the electrons and nuclei, respectively with m_A denoting the mass of nucleus A . The remaining pieces represent the interaction potential V . The third term is the electron-nuclear attraction with Z_A representing the atomic number of nucleus A . The last two terms are the coulombic electron-electron and nuclear-nuclear repulsion.

The molecular wavefunction is complicated by its dependence on nuclear and electronic coordinates. A separation of these coordinates is possible under the Born-Oppenheimer approximation⁵, which assumes the total wavefunction is of the product form

$$\bar{\psi}(\xi) = \psi(r) \chi(R) . \quad (1.10)$$

The electrons are then considered moving in the field of fixed nuclei. Term two of Eq (1.9) then is zero, and the Hamiltonian becomes a function of electronic degrees of freedom at specific nuclear positions. The electronic energy of the system is calculated from the terms of Eq (1.9) which are dependent on electronic coordinates, plus the added contribution of the nuclear-nuclear repulsions.

In this manner, a Born-Oppenheimer potential energy surface may be obtained for the motion of the nuclei under the assumption that the electronic energy is averaged over the electronic wavefunction. Under the Born-Oppenheimer approximation, cross-terms such as $-\frac{1}{2} \frac{\nabla_A \psi(r) \cdot \nabla_A \chi(R)}{m_A}$ are neglected, and consequently the potential energy surface is devoid of information pertaining to the non-adiabatic coupling of nuclei with electrons.

The Representation of the Electronic Wavefunction

It would now seem that a tractable equation for the solution of a many-electron system has been obtained. However, the electron-electron repulsion term in the Hamiltonian prevents a separation of variables of the individual electronic coordinates in the differential equation. The electronic Hamiltonian is hence only analytically soluble for one-electron systems, such as H, He^{+1} , LiH^{+3} , I^{+52} , etc. An approximation to the exact electron interaction is required for treatment of many-electron systems.

To accomplish a separation of electronic coordinates, the exact N-particle electronic wavefunction is most often approximated by N one-particle functions (or orbitals) $\phi(\xi)$, constructed of product form

$$\psi(\xi) \approx \prod_{i=1}^N \phi_i(\xi_i) . \quad (1.11)$$

This wavefunction may in general be complex. However the probability density, which is a modulus-square, is the quantity which is used to relate measurements of the wavefunction to experimental parameters.

Consider a two-particle system $\psi(1, 2)$. Let the system be acted on by a permutation operator P_{12} which interchanges the electronic coordinates of orbitals one and two. A consequence of the modulus square form of the Born interpretation is that the probability density remains invariant whether the wavefunction is symmetric

$$P_{12} \psi(1, 2) = +\psi(1, 2) \quad (1.12)$$

or antisymmetric

$$P_{12} \psi(1, 2) = -\psi(1, 2) \quad (1.13)$$

with respect to permutations. Particles such as electrons behave antisymmetrically, and their wavefunctions will necessarily be so constructed. To maintain the quantum statistics

of the electrons, an antisymmetrized sum of the product wavefunctions is used

$$\psi(\xi) \approx (N!)^{-1/2} \sum_P (-1)^P P \prod_{i=1}^N \phi_i(\xi_i) . \quad (1.14)$$

Equivalently, the many-electron wavefunction is often expressed as the Slater determinant⁶

$$\psi(\xi) \approx (N!)^{-1/2} \begin{vmatrix} \phi_1(\xi_1) & \phi_2(\xi_1) & \dots & \phi_N(\xi_1) \\ \phi_1(\xi_2) & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \phi_1(\xi_N) & \dots & \dots & \phi_N(\xi_N) \end{vmatrix} . \quad (1.15)$$

The determinantal form is antisymmetric, since its sign changes upon interchange of two rows or columns. In addition, the Pauli-Exclusion Principal⁷ follows directly, as the determinant vanishes if any two rows or columns are equivalent. The normalization of Eqs (1.14) and (1.15) ensures that

$$\langle \psi(\xi) | \psi(\xi) \rangle = 1 \quad (1.16)$$

provided that

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} . \quad (1.17)$$

The many-electron state may alternatively be represented through the creation $\{p^\dagger, q^\dagger, \dots\}$ and (Hermitian-conjugate) annihilation $\{p, q, \dots\}$ operators of second-quantization^{8,9}, which have the following properties when acting on the normalized vacuum state

$$\begin{aligned} \langle \phi_p | &= \langle \text{vac} | p & p^\dagger | \text{vac} \rangle &= | \phi_p \rangle \\ \langle \text{vac} | &= \langle \phi_p | p^\dagger & p | \phi_p \rangle &= | \text{vac} \rangle \\ 0 &= \langle \text{vac} | p^\dagger & p | \text{vac} \rangle &= 0 \\ 0 &= \langle \phi_p | p & p^\dagger | \phi_p \rangle &= 0 \end{aligned} \quad (1.18)$$

In second quantization, the one-electron N-particle state is constructed as

$$|\psi(\xi)\rangle = \prod_{i=1}^N i^\dagger |\text{vac}\rangle. \quad (1.19)$$

Properties of the N-particle state are algebraically determined by manipulating the second-quantized operators, using the rule that the creation and annihilation operators obey the following fermionic anticommutation relations

$$\begin{aligned} \langle \text{vac} | [p^\dagger, q^\dagger]_+ | \text{vac} \rangle &= \langle \text{vac} | [p, q]_+ | \text{vac} \rangle = 0 \\ \langle \text{vac} | [p^\dagger, q]_+ | \text{vac} \rangle &= \langle \phi_q | \phi_p \rangle. \end{aligned} \quad (1.20)$$

From the commutation relations, the second-quantized wavefunction is seen to be antisymmetric

$$p^\dagger q^\dagger | \text{vac} \rangle = -q^\dagger p^\dagger | \text{vac} \rangle \quad (1.21)$$

and to contain the Pauli-Exclusion Principal

$$p^\dagger p^\dagger | \text{vac} \rangle = -p^\dagger p^\dagger | \text{vac} \rangle = 0. \quad (1.22)$$

The second-quantized form of the non-relativistic electronic Hamiltonian for fixed nuclei is

$$H = \sum_{p,q} h_{pq} p^\dagger q + \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle p^\dagger q^\dagger s r \quad (1.23)$$

where

$$h_{pq} = -\frac{1}{2} \langle \phi_p | \nabla^2 | \phi_q \rangle - \sum_A Z_A \langle \phi_p | \frac{1}{\mathbf{r} - \mathbf{R}_A} | \phi_q \rangle \quad (1.24)$$

and

$$\langle pq || rs \rangle = \int d\tau_1 d\tau_2 \phi_p^*(1) \phi_q^*(2) \frac{1}{r_{12}} (1 - P_{12}) \phi_r(1) \phi_s(2). \quad (1.25)$$

Unlike the first-quantization version, Eq (1.23) contains no dependence on the number of electrons in the system. The N-dependence of the problem is wholly expressed in the second quantized N-particle reference function, with neutral and ionized states of a molecule represented by the same Hamiltonian.

The Hartree-Fock Equations

In lieu of a direct solution of the Schrödinger equation, an approximate wavefunction can be conveniently obtained using the variation method. This is based on the theorem that for any normalized, well-behaved function $|\Phi\rangle$ which satisfies the boundary conditions of the quantum mechanical problem, it is true that

$$\langle \Phi | \mathcal{H} | \Phi \rangle = \int \Phi^* \mathcal{H} \Phi \, d\tau \geq E_0 , \quad (1.26)$$

where E_0 is the true lowest energy eigenvalue of $\mathcal{H}$. The variation method allows for the minimization of a trial wavefunction with the certainty that this function still represents an upper bound to the exact energy of the system. Although the variation method assures that the trial wavefunction represents an upper bound to the exact energy, it should not be misconstrued that this is an absolute measure of the quality of the trial wavefunction. It is possible in theory to extract all physical properties from the exact wavefunction, and there is no guarantee in the variational theorem that the trial function represents a bound of any kind in the measurement of molecular properties other than the total energy.

Because the approximate wavefunction is a product of single-particle functions, the non-relativistic electronic Hamiltonian in the Born-Oppenheimer approximation is further simplified to a sum of one-electron Fock operators¹⁰⁻¹³

$$F = \sum_{p,q} (h_{pq} + V_{pq}) p^\dagger q = \sum_{p,q} \epsilon_{pq} p^\dagger q , \quad (1.27)$$

where h_{pq} is defined in Eq (1.24) and V_{pq} is the Fock potential, an effective one-electron interaction. The Fock operator is related to the full Hamiltonian by

$$H = F - V + \frac{1}{4} \sum_{p,q,r,s} \langle pq || rs \rangle p^\dagger q^\dagger s r . \quad (1.28)$$

Consider a normalized Hartree-Fock vacuum, which constructs a reference state from eigenfunctions of the Fock operator

$$|0\rangle = \prod_{i=1}^N i^\dagger |HF\rangle . \quad (1.29)$$

To conserve the normality of the second-quantized state, and to facilitate the evaluation of the commutators, the HF orbitals are constrained to be orthonormal

$$\langle HF|[p^\dagger, q]_+|HF\rangle = \delta_{pq} . \quad (1.30)$$

This also simplifies the construction of correlated corrections to the HF state and the determination of the various matrix elements in post-HF studies. The reference state in Eq (1.29) is acted upon by a unitary transformation^{8,9} $e^{i\Lambda}$. The transformation rotates the orbitals among themselves, through the permutation operator Λ

$$\begin{aligned} \Lambda &= \sum_{p,q} \lambda_{pq} p^\dagger q \\ \Lambda^\dagger &= \Lambda \end{aligned} \quad (1.31)$$

and only affects the wavefunction as a phase factor. The transformation is chosen such that the Fock matrix in this basis is diagonal

$$(\mathbf{F})_{pq} = \epsilon^q \delta_{pq} . \quad (1.32)$$

The total energy for the system is measured from the expectation value of the total electronic Hamiltonian in the form of Eq (1.28). The energy remains invariant to the unitary transformation

$$E = \langle 0|H|0\rangle = \langle 0|e^{-i\Lambda}H e^{i\Lambda}|0\rangle . \quad (1.33)$$

By expanding the exponential operators as

$$e^{-i\Lambda}H e^{i\Lambda} = H + i [\Lambda, H] + \frac{i^2}{2!} [\Lambda, [\Lambda, H]] + \dots \quad (1.34)$$

the electronic energy through second-order in Λ is given by

$$E = \langle 0|H|0\rangle + i\langle 0|[\Lambda, H]|0\rangle - \frac{1}{2}\langle 0|[\Lambda, [\Lambda, H]]|0\rangle . \quad (1.35)$$

Because of the variational theorem, a stationary point of the energy may be determined that is assured to be an upper bound. The third term of the right-hand side of Eq (1.35) corresponds to the second derivative or Hessian of the energy hypersurface, which characterizes the stationary point. The form of the Fock potential can be derived from the fact that the first-order variation, or the second term in Eq (1.35), is zero at this point (the Brillouin Condition¹⁴)

$$\langle 0 | [p^\dagger q, H] | 0 \rangle = 0 . \quad (1.36)$$

Using Eqs (1.28) and (1.36), the Fock potential is derived to be

$$V_{ja} = \sum_i \langle ai || ji \rangle . \quad (1.37)$$

Equation (1.37) reveals that only the occupied-virtual portion of the electron interaction is determined from the Brillouin condition. There is a degree flexibility in choice for the occupied-occupied and virtual-virtual blocks of the Fock potential. To give physical significance to the diagonal Fock-matrix elements as the approximate ionization potential for an occupied orbital and electron affinity for an unoccupied orbital (Koopmans' Theorem¹⁵), these blocks are normally chosen so that the Fock potential has the more general operator form

$$V_{pq} = \sum_i \langle pi || qi \rangle p^\dagger q . \quad (1.38)$$

The coulombic term in Eq (1.38) (defined as the unpermuted form of two-electron integral in Eq (1.25)) would be the only contribution to the potential if the wavefunction is assumed to be strictly a (Hartree) product form^{10,11}

$$V_{pq}(\xi_1) = \langle p | \sum_i \int d\tau_2 \frac{|\phi_i(\xi_2)|^2}{r_{12}} | q \rangle . \quad (1.39)$$

From Eq (1.39), a physical interpretation for the coulombic term can be rationalized as follows. In the Hartree procedure, the exact electron interaction is replaced with a

mean field repulsion. The potential experienced by an electron occupying orbital q is the classical coulombic repulsion generated from the probability (charge) densities of all occupied electronic orbitals. This effective one-electron operator allows the separation of the individual electronic coordinates, but there is a linear dependence of the wavefunction of each electron on the probability density of all others. This suggests a recursive procedure where the one-electron wavefunctions or orbitals obtained at each iteration construct the average electronic interaction potential for the next cycle.

The unoccupied or virtual orbitals determined from the Fock potential of Eq (1.39) are constructed with respect to a psuedo-electron under the influence of the actual N electrons of the system. Although the connection with electron affinity is obvious, using a virtual orbital as a replacement in the ground state determinant is a crude representation of an excited state. Because of the Brillouin condition, the total electronic ground state is stable with respect to the single replacement determinants but, as will become apparent in later chapters, linear combinations of these functions do provide the leading corrective terms for the excited state representation.

The exchange portion (the permuted form of two-electron integral in Eq (1.25)) has no classical analog. From its sign in the Fock expression, the exchange integral is seen to have a relaxation effect on the molecular energy. This exchange is a direct consequence of the antisymmetry of the product wavefunction employed in the HF method^{12,13}. The exchange operator is non-local, meaning it cannot be written in a probability density form similar to Eq (1.39).

The HF state is related to the vacuum state by a basis

$$\begin{aligned} p^\dagger &= \sum_{\nu} c_{\nu}^p \nu^\dagger \\ q &= \sum_{\mu} c_{\mu}^{q*} \mu . \end{aligned} \tag{1.40}$$

The anticommutation relation for the basis set is

$$\begin{aligned} \langle HF|[p^\dagger, q]_+|HF\rangle &= \langle \phi_q|\phi_p\rangle = \\ \sum_{\mu,\nu} c_\mu^{q*} c_\nu^p \langle \text{vac} | [\nu^\dagger, \mu]_+ | \text{vac} \rangle &= \sum_{\mu,\nu} c_\mu^{q*} c_\nu^p \langle \chi_\mu | \chi_\nu \rangle = \sum_{\mu,\nu} c_\mu^{q*} c_\nu^p S_{\mu\nu} . \end{aligned} \quad (1.41)$$

Introducing this basis into the orthonormality condition (Eq (1.30)), and applying this constraint to the canonical Fock matrix of Eq (1.32) leads to the following equations for the transformed state

$$\begin{aligned} \sum_{\mu,\nu} c_\mu^{q*} F_{\mu\nu} c_\nu^p &= \sum_{\mu,\nu} c_\mu^{q*} S_{\mu\nu} c_\nu^p \epsilon^p \\ \sum_{\mu} c_\mu^{q*} \left[\sum_{\nu} F_{\mu\nu} c_\nu^p - S_{\mu\nu} c_\nu^p \epsilon^p \right] &= 0 . \end{aligned} \quad (1.42)$$

Since the coefficients c_μ^{q*} and c_ν^p are independent, the quantity in brackets of Eq (1.42) must be zero. The matrix form of this condition is the Roothaan equations¹⁶

$$\mathbf{FC}^p = \mathbf{SC}^p \epsilon^p . \quad (1.43)$$

Under the assumption of a closed-shell system with all orbitals doubly occupied, a general element of the Fock-matrix is evaluated from Eqs (1.27), (1.38), and (1.40) to be

$$\begin{aligned} F_{\mu\nu} &= h_{\mu\nu} + \sum_{\sigma,\lambda} P_{\sigma\lambda} \left[\langle \mu\lambda | \nu\sigma \rangle - \frac{1}{2} \langle \mu\lambda | \sigma\nu \rangle \right] \\ P_{\sigma\lambda} &= 2 \sum_i c_\sigma^i c_\lambda^{i*} . \end{aligned} \quad (1.44)$$

The dependence of the Fock potential on the probability density of the occupied orbitals is expressed through the coefficients c in the density matrix. Since the density matrix itself is constructed from the coefficients of expansion of the basis, the iterative solution of Eq (1.43) is required.

The independent electron ansatz is applied extensively at both the instructional and research level of all the various chemistry disciplines, as a means of qualitative analysis

and descriptive modelling of chemical phenomena. In this section, the HF SCF method has been used to achieve a separation of electronic variables by employing an effective one-electron interaction potential to the non-relativistic Born-Oppenheimer Hamiltonian. The canonical Hartree-Fock approximation should be viewed as a mathematical construct of the independent particle concept, and—provided the basis of atomic states is correctly represented—its applicability to a particular chemical problem indicates the validity of the molecular orbital model in that context.

The Intermediate Neglect of Differential Overlap

The solution of the Roothaan equations will require evaluation of the elements of the one-electron matrix $\mathbf{h}$ and of the metric matrix $\mathbf{S}$, along with the two-electron integrals. Then for each SCF iteration, a partial two-electron transform and a diagonalization step must also be performed. A procedure which explicitly calculates all possible integrals which enter the HF procedure is known as *ab initio*. Ignoring redundancies arising from real orbitals and permutation symmetry, there are roughly N^4 two-electron repulsion integrals. In normal computing environments, these are too numerous to hold in fast storage or Random Access Memory (RAM), so they must be kept externally and input when specifically required to construct a new Fock potential or for use in post-SCF procedures. For extended systems, the storage requirements and integral calculations become prohibitive.

To accomplish a reduction in the number of integrals which are to be calculated, and to augment their evaluation, a class of SCF theories has been developed which logically incorporates experimental data. These methods are termed “semiempirical”, because of an attempt to correlate the SCF method with empirical data for meaningful interpretation, while reducing the computation requirement of the Fock matrix to an N^2 procedure. The wavefunction obtained in this manner will hopefully have the proper features that allow

for a reasonable description of a molecule and its properties, at a reduced expense of time and effort as compared to the *ab-initio* wavefunction. The applications of this dissertation will provide a test of the validity of this premise.

To reduce the overall effort of the SCF procedure, the semiempirical methods begin by explicitly treating only the valence electrons contributed by a particular atom. This idea is used extensively in chemistry, e.g. reaction mechanisms, crystal field theory, acid-base theory, chelation, etc. Hückel¹⁷⁻¹⁹ calculations, which exploit the topology of conjugated systems, remain popular for application to aromatic molecules. Calculations of this type include only the π -electrons of the system. In certain cases, it is advantageous to eliminate explicit consideration of core electrons. Specifically, in molecules containing heavy atoms where relativistic effects become non-negligible, *ab-initio* methods must realistically be replaced by methods including effective core potentials.

The valence-only methods to be considered are based on the Zero Differential Overlap (ZDO) approximation²⁰. For one-electron property integrals, ZDO assigns the probability density of two basis functions in the infinitesimal volume element $d\tau$ as

$$d\tau|\chi_\mu\chi_\nu^*| = d\tau|\chi_\mu\chi_\mu^*|\delta_{\mu\nu} . \quad (1.45)$$

Under the ZDO restriction, the elements of the metric become

$$S_{\mu\nu} = \delta_{\mu\nu} , \quad (1.46)$$

and form a unit matrix

$$S = 1 . \quad (1.47)$$

The matrix elements which enter into the one-electron portion of the Fock matrix are determined as follows. The diagonal elements given the designation $U_{\mu\mu}^A$ represent

the kinetic energy of an electron in orbital k and the attraction by its own core A . This is obtained using the value^{21,22}

$$U_{ss}^H = -IP, \quad (1.48)$$

the ionization potential for hydrogenic centers, and otherwise

$$\begin{aligned} U_{ss}^A &= -(IP_s) - (Z_A^* - 1)\Gamma_{ss} + \frac{1}{6} \left(Z_A^* - \frac{3}{2} \right) G^1 \\ U_{pp}^A &= -(IP_p) - (Z_A^* - 1)\Gamma_{AA} + \frac{1}{3}G^1 + \frac{2}{25} \left(Z_A^* - \frac{5}{2} \right) F^2. \end{aligned} \quad (1.49)$$

The above equations use the definition of Z_A^* as the effective core charge of center A and also contain other terms which will be described in the following text. The term $V_{\mu\mu}^B$ is subtracted from the diagonal elements of the one-electron matrix. This represents the attraction of electron μ by the other cores B and has the value

$$V_{\mu\mu}^B = Z_B^* \Gamma_{AB}. \quad (1.50)$$

For the standard parameterizations of the Complete Neglect of Differential Overlap (CNDO) and Intermediate Neglect of Differential Overlap (INDO) approximations, the off-diagonal elements of the one-electron matrix are calculated according to

$$h_{\mu\nu} = S_{\mu\nu} (\beta^A + \beta^B) / 2 \quad (1.51)$$

using the overlap matrix and the bonding parameter β^{23} .

For CNDO²⁴, the two-electron integrals are determined from a strict application of ZDO

$$\langle \mu\nu | \sigma\lambda \rangle = \langle \mu\nu | \mu\nu \rangle \delta_{\mu\sigma} \delta_{\nu\lambda}. \quad (1.52)$$

The INDO two-electron approximation retains all one-center exchange integrals, in order to overcome the gross oversimplification associated with their neglect in CNDO. For s- and p-types, the standard INDO parameterization²⁵ of the two-electron integrals are

$$\begin{aligned}
\Gamma_{AA} &= \langle s_A s_A | s_A s_A \rangle \\
\Gamma_{MN} (\langle s s | p_x p_x \rangle) &= \frac{1}{3} G^1 \\
\Gamma_{MN} (\langle p_x p_x | p_y p_y \rangle) &= \frac{3}{25} F^2 \\
\Gamma_{MN} (\langle p_x p_x | p_x p_x \rangle) &= \Gamma_{AA} + \frac{4}{25} F^2 \\
\Gamma_{MN} (\langle p_x p_y | p_x p_y \rangle) &= \Gamma_{AA} - \frac{2}{25} F^2 .
\end{aligned} \tag{1.53}$$

The value Γ_{AA} is determined using s-type Slater functions, and the values G^1 and F^2 were obtained empirically from the electronic spectra of the corresponding atoms.

The above implementation of INDO is intended to mimic *ab-initio* HF calculations, and is used primarily for INDO geometry optimizations. There is an alternative parameterization scheme, INDO/Spectroscopic (INDO/S)²⁶⁻²⁸, which is an extension of the CNDO/S model²⁹⁻³¹. The INDO/S method has proven very successful for the determination of the energy of excited states, and hence their UV spectra. These states are constructed from the singly-excited Configuration Interaction (CI) method (see Chapter 2). In INDO/S, the term Γ_{AA} is calculated as the difference between the ionization potential and the electron affinity for the electron. The off-diagonal one-electron matrix elements are given the form³²

$$\begin{aligned}
\Gamma_{AA} &= IP - EA \\
h_{\mu\nu} &= \frac{1}{2} (\beta'_A + \beta'_B) (S_{\mu\sigma\nu\sigma} K_{\sigma\sigma} + S_{\mu\sigma\nu\pi} K_{\pi\pi} + S_{\mu\sigma\nu\delta} K_{\delta\delta} + \dots)
\end{aligned} \tag{1.54}$$

where the value $K_{\sigma\sigma}$ is a weighting factor for the sigma-type interactions of the orbitals and $S_{\mu\sigma\nu\sigma}$ represents the sigma-type overlap between the basis functions μ and ν . The interaction factors are crucial for the proper description of relative molecular orbital energies. The two-electron integrals are calculated using the Mataga-Nishimoto formula³³

$$\Gamma_{MN} = \frac{\kappa}{\frac{2\kappa}{\Gamma_{AA} + \Gamma_{BB}} + r_{AB}} \tag{1.55}$$

with the value of κ assigned 1.2.

It is relevant to discuss the implications of the ZDO and valence-only restrictions on the Roothaan equations. With respect to ZDO, the above discussion indicates that in many cases the use of experimental or wholly empirical parameters allows the justification of a unit metric. But in some instances, STO functions have been used to evaluate elements of the Fock matrix. It will also be necessary to define some sort of basis set in order to determine property integrals. A formal basis of STO functions may be rationalized as implicit in the Roothaan equations under the transformations

$$\begin{aligned} \mathbf{F}' &= \mathbf{S}^{-1/2} \mathbf{F} \mathbf{S}^{-1/2} \\ \mathbf{C}' &= \mathbf{S}^{1/2} \mathbf{C} \end{aligned} \quad (1.56)$$

with respect to a metric formed using STOs. Equation (1.43) then simplifies to

$$\mathbf{F}' \mathbf{C}' = \mathbf{C}' \epsilon . \quad (1.57)$$

When the Fock matrix is real, the coefficients $\mathbf{C}'$ are elements of an orthogonal transformation matrix

$$\mathbf{C}'^T \mathbf{C}' = \mathbf{C}^T \mathbf{S}^{1/2} \mathbf{S}^{1/2} \mathbf{C} = \mathbf{1} . \quad (1.58)$$

This leads directly to a more physical interpretation for the density matrix. The sum of the probability densities of the one-electron HF orbitals integrated over all space yields the number of electrons of a system

$$\sum_i \int |\phi_i \phi_i^*| d\tau = N . \quad (1.59)$$

Substitution of the non-orthogonal basis expansion in Eq (1.59) leads to

$$N = \sum_{\mu\nu} P_{\mu\nu} S_{\nu\mu} = \text{tr}(\mathbf{P}\mathbf{S}) . \quad (1.60)$$

The i^{th} diagonal element of the trace matrix is known as the Mulliken population²³ of orbital i , and is interpreted as the number of electrons associated with this orbital. The density matrix in the orthogonal basis becomes

$$\mathbf{P} = \mathbf{C} \mathbf{n} \mathbf{C}^T = \mathbf{S}^{-1/2} \mathbf{C}' \mathbf{n} \mathbf{C}'^T \mathbf{S}^{-1/2} \quad (1.61)$$

Using the orthogonal density matrix and permutation of the trace-product, Eq (1.60) becomes

$$N = \text{tr} \left(\mathbf{S}^{-1/2} \mathbf{C}' \mathbf{n} \mathbf{C}'^T \mathbf{S}^{-1/2} \mathbf{S} \right) = \text{tr} \left(\mathbf{C}' \mathbf{n} \mathbf{C}' \right) = \text{tr} \mathbf{P}' . \quad (1.62)$$

The diagonal elements of the orthogonal density matrix give directly the electron populations for each orbital, while the off-diagonal elements are interpreted to indicate the electron sharing and hence bonding character of the two orbitals. This interpretation is the Löwdin population analysis^{34,35}. The orthogonal density matrix is also often referred to as the charge and bond order matrix.

Under the assumption that an STO atomic orbital basis is inherent to the INDO method, an inconsistency is encountered in the formation of the Fock operator. It would be rigorous to employ the density matrix as defined in Eq (1.44) in constructing the Fock matrix elements. In practice, the INDO basis is assumed to be the Löwdin orthogonal set³⁴

$$\chi' = \chi \mathbf{S}^{-1/2} \quad (1.63)$$

for justification of the use of the orthogonal density in construction of the Fock matrix. The Löwdin orthogonal and canonical transformations of basis are completely congruent

$$\chi' \mathbf{C}' = \chi \mathbf{S}^{-1/2} \mathbf{S}^{1/2} \mathbf{C} = \chi \mathbf{C} . \quad (1.64)$$

The implication of the valence-only approximation on Eq (1.57) is that the Roothaan equations take on a block-diagonal form³⁶

$$\begin{bmatrix} \mathbf{F}'_{\text{core}} & \mathbf{0} \\ \mathbf{0} & \mathbf{F}'_{\text{val}} \end{bmatrix} \begin{bmatrix} \mathbf{C}'_{\text{core}} & \mathbf{0} \\ \mathbf{0} & \mathbf{C}'_{\text{val}} \end{bmatrix} = \begin{bmatrix} \mathbf{C}'_{\text{core}} & \mathbf{0} \\ \mathbf{0} & \mathbf{C}'_{\text{val}} \end{bmatrix} \begin{bmatrix} \epsilon_{\text{core}} & \mathbf{0} \\ \mathbf{0} & \epsilon_{\text{val}} \end{bmatrix} . \quad (1.65)$$

The core expression is assumed to be completely separable and in relative measurements, such as computation of electronic spectra, does not enter into the problem at all. In geometry optimization, the core energy is estimated as

$$E_{\text{core}} = \frac{Z_A^C Z_B^C}{r_{AB}} . \quad (1.66)$$

INTRODUCTION

The approaches to be used for calculating molecular properties are presented in this chapter. Model theories relevant to the study of stationary state or time-dependent phenomena are first derived in terms of the response of the wavefunction describing the system. Since the wavefunctions cannot be rigorously determined, it will then be necessary to introduce the HF approximation and its extensions to evaluate the expressions for molecular properties. The equations for time-independent perturbations of a stationary state system are developed in the framework of Rayleigh-Schrödinger Perturbation Theory (RSPT). The response of a system influenced by a time-varying perturbation is next derived from Green's function techniques, using the formal theory of propagators. The Tamm-Dancoff Approximation (TDA) and the Random Phase Approximation (RPA) are then introduced as state representations. Finally, the RPA method is shown to be a consistent basis for the moment expansion of the propagator.

Rayleigh-Schrödinger Perturbation Theory

In the laboratory, a molecular property is measured by probing a system, e.g., with an electric field to determine polarizabilities, a magnetic field for susceptibilities, or electromagnetic radiation for spectroscopic parameters. In theory, any observable quantity can be calculated by collapsing the exact wavefunction for a system into a particular eigenstate. To induce the correct eigenstate from the exact wavefunction, a technique will be used which is not unlike an experiment—the system will be probed with a perturbation. The energy parameters which represent the moment expansions of

molecular response may in this manner be extracted in a most convenient fashion. In this section, the theoretical “probe” will be a static time-independent event. The evaluation of molecular properties which are influenced by time-varying phenomena is the subject of the next section.

To apply time-independent perturbation theory, the total Hamiltonian for a system is partitioned into a zeroth-order term H_0 and a term which contains the perturbation

$$\mathcal{H} = H_0 + V . \quad (2.1)$$

The perturbation V in this case represents the stimulus of the experimental probe. It is often also employed to compensate the zeroth order Hamiltonian for an inherent deficiency— such as the fluctuation potential

$$V = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle (p^\dagger q^\dagger s r - \langle 0 | q^\dagger s | 0 \rangle p^\dagger r) , \quad (2.2)$$

which corrects the independent particle zeroth-order HF Hamiltonian $H_0 = \sum_{p,q} F_{pq}$ with the proper many-body electron correlation³⁷.

It is assumed there exists a complete orthonormal set of zeroth-order eigenstates

$$\begin{aligned} H_0 |n\rangle &= E_n^{(0)} |n\rangle \\ |n\rangle &\in |\mathcal{N}\rangle . \end{aligned} \quad (2.3)$$

In general, the perturbation expansion may be defined with respect to any of the states in the zeroth-order manifold, subject to the restriction that this state be non-degenerate in energy. The formalism is to be developed here explicitly as ground state perturbation theory, relative to the state of lowest energy denoted $|k\rangle$. Non-linear effects, resulting from the relaxation under the perturbing influence of V , will be measured— assuming the proper normalization— as a transition integral of the unperturbed function $|k\rangle$ with the response wavefunction $|\Phi_k\rangle$. The response wavefunction will be constructed using the wave reaction or resolvent operator^{38,39}. The resolvent is particularly utile in highlighting the important aspects of this form of perturbation theory.

The response wavefunction is introduced as an eigenfunction of the total Hamiltonian

$$\mathcal{H}|\Phi_k\rangle = E_k|\Phi_k\rangle \quad (2.4)$$

and carries the subscript k because of its intermediate normalization with $|k\rangle$

$$\langle k|\Phi_k\rangle = 1 . \quad (2.5)$$

In state vector language, $|\Phi_k\rangle$ is constructed with unit projection along $|k\rangle$

$$\begin{aligned} P_{\mathcal{N}}|\Phi_k\rangle &= |k\rangle \\ P_{\mathcal{N}} &= |k\rangle\langle k| . \end{aligned} \quad (2.6)$$

The response wavefunction can be expressed in an order-by-order fashion

$$|\Phi_k\rangle = \sum_{n=0}^{\infty} |\Phi_k^{(n)}\rangle \quad (2.7)$$

starting with $|\Phi_k^{(0)}\rangle = |k\rangle$. The higher corrections $|\Phi_k^{(n)}\rangle$ are projected from $|\Phi_k\rangle$ according to

$$|\Phi_k\rangle = |k\rangle + Q_{\mathcal{N}}|\Phi_k\rangle \quad (2.8)$$

via a projection operator which is complementary to the ground state

$$Q_{\mathcal{N}} \equiv \sum_{n \neq k} |n\rangle\langle n| . \quad (2.9)$$

The projection operators are idempotent

$$\begin{aligned} Q_{\mathcal{N}}^2 &= Q_{\mathcal{N}} \\ P_{\mathcal{N}}^2 &= P_{\mathcal{N}} \end{aligned} \quad (2.10)$$

and span the space of the zeroth-order eigenfunctions

$$P_{\mathcal{N}} + Q_{\mathcal{N}} = 1_{\mathcal{N}} . \quad (2.11)$$

Using the Hamiltonian of Eq (2.1), an energy parameter $\mathcal{E}$ is added to both sides of Eq (2.4), which leads to

$$(\mathcal{E} - H_0) |\Phi_k\rangle = (\mathcal{E} - E_k + V) |\Phi_k\rangle . \quad (2.12)$$

Assigning the arbitrary energy parameter the value $E_k^{(0)}$ defines the sequence known as Rayleigh-Schrödinger Perturbation Theory (RSPT). If the parameter is chosen so that $\mathcal{E} = E_k$, the Brillouin-Wigner perturbation series is obtained⁴⁰.

Since the projection operator $Q_{\mathcal{N}}$ commutes with the zeroth-order Hamiltonian, the RSPT expression for $Q_{\mathcal{N}}|\Phi_k\rangle$ is derived from Eq (2.12) to be

$$Q_{\mathcal{N}}|\Phi_k\rangle = \left(E_k^{(0)} - H_0\right)^{-1} Q_{\mathcal{N}} \left(E_k^{(0)} - E_k + V\right) |\Phi_k\rangle . \quad (2.13)$$

Equation (2.13) is rewritten by multiplying both sides by $Q_{\mathcal{N}}$ and using Eq (2.10)

$$Q_{\mathcal{N}}|\Phi_k\rangle = R_{\mathcal{N}} \left(E_k^{(0)} - E_k + V\right) |\Phi_k\rangle . \quad (2.14)$$

The resolvent or wave reaction operator has been defined in Eq (2.14)

$$R_{\mathcal{N}} = \sum_{m, n \neq k} |m\rangle\langle m| \left(E_k^{(0)} - H_0\right)^{-1} |n\rangle\langle n| . \quad (2.15)$$

Because of the orthonormality of the zeroth-order basis states, the resolvent is unequivocally written as

$$R_{\mathcal{N}} = \sum_{n \neq k} |n\rangle\langle n| \left(E_k^{(0)} - H_0\right)^{-1} |n\rangle\langle n| . \quad (2.16)$$

It is evident at this point that the ground state function $|k\rangle$ must be non-degenerate in energy with any state of the orthogonal complement, or a singularity is encountered in the wave reaction operator.

Equation (2.14) is substituted directly into Eq (2.8)

$$|\Phi_k\rangle = |k\rangle + R_{\mathcal{N}} \left(E_k^{(0)} - E_k + V\right) |\Phi_k\rangle . \quad (2.17)$$

Iterating Eq (2.17) gives the infinite-order expansion of the response wavefunction

$$|\Phi_k\rangle = \sum_{n=0}^{\infty} \left[R_N \left(E_k^{(0)} - E_k + V \right) \right]^n |k\rangle. \quad (2.18)$$

The convergence of the infinite order sum is contingent upon the partitioning of $\mathcal{H}$

$$H_0 \gg V. \quad (2.19)$$

By multiplying Eq (2.4) with $\langle k|$ and using Eq (2.18), the energy through any order n can be isolated

$$E_k^{(n)} - E_k^{(0)} = \langle k|V|\Phi_k^{(n-1)}\rangle. \quad (2.20)$$

According to Eq (2.20), the n^{th} -order value of the energy will in general have the form of a transition integral between the ground state $\langle k|$ and the response state $|\Phi_k^{(n-1)}\rangle$. This may be stated in a manner to connect with the preliminary discussion of this section—the response wavefunction $|\Phi_k\rangle$ must be forced into the intermediately normalized eigenstate $|\Phi_k^{(n-1)}\rangle$ to observe the n^{th} -order moment of the energy.

Starting with the zeroth-order wavefunction, the first-order energy is then obtained from Eq (2.20) as the expectation value for the perturbing operator with the ground state

$$E_k^{(1)} = \langle k|V|\Phi_k^{(0)}\rangle = \langle k|V|k\rangle. \quad (2.21)$$

The first-order perturbed wavefunction is given from Eq (2.18) as

$$|\Phi_k^{(1)}\rangle = R_N V |k\rangle. \quad (2.22)$$

In Eq (2.22), the orthonormality of the zeroth-order eigenfunctions $\langle n|k\rangle = 0$ has been used. The second-order energy is then

$$E_k^{(2)} = \langle k|V|\Phi_k^{(1)}\rangle = \langle k|V R_N V |k\rangle. \quad (2.23)$$

The familiar sum-over-states form for Eq (2.23) is obtained when the resolvent operator is specifically introduced

$$E_k^{(2)} = \sum_{n \neq k} \frac{\langle k|V|n\rangle \langle n|V|k\rangle}{E_k^{(0)} - E_n^{(0)}}. \quad (2.24)$$

The second correction to the perturbed eigenstate is

$$|\Phi_k^{(2)}\rangle = R_{\mathcal{N}} \left(V - E_k^{(1)} \right) R_{\mathcal{N}} V |k\rangle \quad (2.25)$$

and gives the energy at third-order to be

$$E_k^{(3)} = \langle k | V R_{\mathcal{N}} V R_{\mathcal{N}} V | k \rangle - E_k^{(1)} \langle k | V R_{\mathcal{N}}^2 V | k \rangle . \quad (2.26)$$

The second piece of the right-hand side of Eq (2.26) is the renormalization or Exclusion-Principal Violation (EPV) term, which cancels against the “unlinked” portion of the first term. Similar terms also arise at higher order and keep the energy expression extensive with the number of particles in the system³⁷. The third-order sum-over-states expression is given as

$$\begin{aligned} E_k^{(3)} = & \sum_{n,m \neq k} \frac{\langle k | V | n \rangle \langle n | V | m \rangle \langle m | V | k \rangle}{\left(E_k^{(0)} - E_n^{(0)} \right) \left(E_k^{(0)} - E_m^{(0)} \right)} \\ & - E_k^{(1)} \sum_{n \neq 0} \frac{|\langle k | V | n \rangle|^2}{\left(E_k^{(0)} - E_n^{(0)} \right)^2} . \end{aligned} \quad (2.27)$$

The odd orders of the energy expansion can be used as examples of the 2N+1 rule of perturbation theory, which states that the Nth order wavefunction is sufficient to calculate the perturbative energy through order 2N+1. For the case when N=0, the first-order energy is obtained from the zeroth-order wavefunction. In the instance that N=1, the first-order wavefunction is sufficient to determine the third-order energy. This is demonstrated by direct substitution of Eq (2.22) into Eq (2.26)

$$E_k^{(3)} = \langle \Phi_k^{(1)} | V | \Phi_k^{(1)} \rangle - E_k^{(1)} \langle \Phi_k^{(1)} | \Phi_k^{(1)} \rangle . \quad (2.28)$$

Equation (2.28) shows the renormalization term is a consequence of the choice of intermediate normalization

$$\begin{aligned}\langle k|\Phi_k\rangle &= 1 = \langle k|k\rangle + \langle k|\Phi_k^{(1)}\rangle + \langle k|\Phi_k^{(2)}\rangle + \cdots \\ &= 1 + 0 + 0 + \cdots .\end{aligned}\tag{2.29}$$

The EPV term corrects for the fact that the first-order perturbed wavefunction need not necessarily be normalized.

The Propagator

The response properties of a system under the influence of a time varying perturbation, such as the interaction of radiation with matter, are most elegantly treated using propagator theory⁸. The study begins by returning to the time-dependent Schrödinger equation, with the potential for interaction of the form $\mathcal{V}(\xi, t)$. A separation of the coordinate space and the time variable is not rigorous in this case. With the Hamiltonian for the system explicitly time-dependent, there are no strictly stationary states, or the probability density for the wavefunction is not time independent. For the prototype interaction—the excitation of a system by a varying electric field—the initial state of a system will be approximated as an eigenfunction of a time-independent Hamiltonian H_0 . Under the influence of the perturbation, the system is observed again by measuring a physical property. Upon making the measurement, it is found that the oscillating perturbation propagates a disturbance in the probability density, which is proportional to the frequency of the applied field.

In the discussion that follows, the total Hamiltonian will be explicitly treated semi-classically (molecule quantized, radiation not quantized). This assumption is acceptable provided that the wavelength of the perturbation is large with respect to molecular dimension.

Since the perturbation explicitly contains time, the wavefunction solves the time-dependent Schrödinger equation

$$(H_0 + \mathcal{V}) |\Psi(\xi, t)\rangle = i \frac{d|\Psi(\xi, t)\rangle}{dt} . \quad (2.30)$$

The total Hamiltonian is partitioned such that the time-dependence of the problem is wholly contained in the interaction potential $\mathcal{V}$. A state vector is defined according to

$$|\Psi(\xi, t)\rangle = e^{iH_0 t} |\Psi_k(\xi, t)\rangle , \quad (2.31)$$

such that at $t = -\infty$, the function $|\Psi_k(\xi, t)\rangle$ coalesces with the zeroth-order time-independent ground state wavefunction $|k\rangle$. According to the quantum mechanical principal of causality⁴¹, the state vector $|\Psi(\xi, t)\rangle$ evolves as a time-dependent unitary transformation of the initial state $|\Psi_k(\xi, t)\rangle$.

The probability density operator for the time-evolved state is written

$$\rho'_k(t) = e^{iH_0 t} |\Psi_k\rangle \langle \Psi_k| e^{-iH_0 t} . \quad (2.32)$$

The equation of motion for this density operator is

$$\frac{d\rho'_k(t)}{dt} = e^{iH_0 t} \left[\frac{d|\Psi_k\rangle}{dt} \langle \Psi_k| + |\Psi_k\rangle \frac{d\langle \Psi_k|}{dt} \right] e^{-iH_0 t} + i [H_0, \rho'_k(t)] . \quad (2.33)$$

Using Eq (2.30), the equation of motion becomes

$$i \frac{d\rho'_k(t)}{dt} = [\mathcal{V}', \rho'_k(t)] \quad (2.34)$$

where

$$\mathcal{V}' = e^{iH_0 t} \mathcal{V} e^{-iH_0 t} . \quad (2.35)$$

This quantum mechanical representation is the interaction picture. It is an intermediate between the Heisenberg formalism⁴²— in which the operators are time-dependent and the state vectors are time-independent— and the Schrödinger development¹⁻⁴— where the opposite is true. In the interaction picture, the motion of the state vector, or the

propagation of the state density, is dictated by the perturbation $\mathcal{V}'$. Equation (2.34) is also known as the Liouvillian⁴³ of the density. The initial condition for the density is

$$\lim_{t \rightarrow -\infty} \rho'_k(t) = \lim_{t \rightarrow -\infty} e^{iH_0 t} |\Psi_k\rangle \langle \Psi_k| e^{-iH_0 t} = e^{iH_0 t} |k\rangle \langle k| e^{-iH_0 t} = |k\rangle \langle k| = \rho_k(0) . \quad (2.36)$$

Integration of Eq (2.34) gives

$$\rho'_k(t) = \rho_k(0) - i \int_{-\infty}^t [\mathcal{V}'(t'), \rho'_k(t')] dt' . \quad (2.37)$$

This may be solved order-by-order by inserting the ground state density as a first approximation into the commutator, and iterating. At zeroth order, the time-evolved density is approximated by that for the initial ground state $|k\rangle$. At first-order, the linear response function is then given by

$$\rho'(t) = \rho_k(0) - i \int_{-\infty}^t [\mathcal{V}'(t'), \rho_k(0)] dt' . \quad (2.38)$$

Equation (2.38) may be transformed to the Schrödinger picture by the left-multiplication with $e^{-iH_0 t}$ and right-multiplication by $e^{iH_0 t}$

$$\rho_k(t) = |\Psi_k\rangle \langle \Psi_k| = \rho_k(0) - i \int_{-\infty}^t [\mathcal{V}'(t' - t), \rho_k(0)] dt' . \quad (2.39)$$

Equation (2.39) uses the Hermiticity of H_0 to commute the exponential operator with $\rho_k(0)$.

An arbitrary property of the system is measured as usual from the density, by calculating the expectation value of the proper quantum mechanical operator. For an observable relative to the linear response of the time-varying perturbation, the state average value is determined using the density of the form in Eq (2.39)

$$\begin{aligned} \langle \Psi_k | \hat{A} | \Psi_k \rangle &= \text{tr} \left(\rho_k(t) \hat{A} \right) = \\ &= \text{tr} \left(\rho_k(0) \hat{A} \right) - i \int_{-\infty}^t \text{tr} \left[\mathcal{V}'(t' - t) \rho_k(0) \hat{A} - \rho_k(0) \mathcal{V}'(t' - t) \hat{A} \right] dt' . \end{aligned} \quad (2.40)$$

Using the cyclic invariance of the trace product, the linear response average value of $\hat{A}$ becomes

$$\langle \Psi_k | \hat{A} | \Psi_k \rangle = \text{tr} \left(\rho_k(0) \hat{A} \right) + \int_{-\infty}^{\infty} \langle \langle \hat{A}; \mathcal{V}'(t' - t) \rangle \rangle dt'. \quad (2.41)$$

In Eq (2.41), the retarded double-time Green's function⁴⁴ has been introduced

$$\langle \langle \hat{A}; \mathcal{V}'(t' - t) \rangle \rangle = -i\Theta(t - t') \langle k | [\hat{A}, \mathcal{V}'(t' - t)] | k \rangle \quad (2.42)$$

with $\Theta(t - t')$ defined as the Heaviside step function

$$\Theta(t - t') = \begin{cases} 1, & t > t', \\ 0, & t' > t. \end{cases} \quad (2.43)$$

In this case, the operators representing $\hat{A}$ and $\mathcal{V}'$ are both assumed to be number-conserving (boson-like). The Green's function of Eq (2.42) is therefore expressed as a commutator and is called the polarization propagator⁴⁵⁻⁴⁷. For fermionic, non-conserving operators, the Green's function would contain an anti-commutator, and is named the electron propagator^{48,49}. In Eq (2.41), the state-average value of $\hat{A}$ is computed as the expectation value at $t = -\infty$, plus the integral relative to an external perturbation describing how the response propagates from time $t' < t$ through the system.

The external perturbation to be studied in this application of the theory of propagators will be an oscillating electric field⁵⁰

$$\mathcal{V}(t) = - \int_{-\infty}^{\infty} d\omega \mathbf{r} \bullet \mathbf{E}(\omega) e^{-i\omega t + \varepsilon t}. \quad (2.44)$$

The infinitesimal ε ensures that $\mathcal{V}(-\infty) = 0$. The polarization propagator will be used to measure the linear response of the dipole moment

$$\hat{A} = \mathbf{r} \quad (2.45)$$

induced in the system. Inserting Eq (2.45) into Eq (2.41), along with the interaction representation of Eq (2.44), it is found that

$$\mu_{\alpha}(t) = \mu_{\alpha}(0) - \int_{-\infty}^{\infty} d\omega \sum_{\beta} \int_{-\infty}^{\infty} dt' \langle \langle r_{\alpha}; r'_{\beta}(t' - t) \rangle \rangle E_{\omega\beta} e^{-i\omega t' + \varepsilon t'} \quad (2.46)$$

where the Greek indices of the position operators imply the Cartesian values x, y, and z. With a change of variable $s = t' - t$, this is written

$$\mu_{\alpha}(t) = \mu_{\alpha}(0) - \int_{-\infty}^{\infty} d\omega \sum_{\beta} \int_{-\infty}^{\infty} ds \langle \langle r_{\alpha}(0); r'_{\beta}(s) \rangle \rangle e^{-i\omega s + \varepsilon s} E_{\omega\beta} e^{-i\omega t + \varepsilon t}. \quad (2.47)$$

Comparing Eq (2.47) with the conventional expression for the periodic induced dipole moment⁵⁰

$$\mu_{\mathbf{I}}(\mathbf{t}) = \int_{-\infty}^{\infty} d\omega \alpha(\omega) \mathbf{E}_{\omega} e^{-i\omega t + \varepsilon t} \quad (2.48)$$

allows the following identification for the dynamic dipole polarizability

$$\alpha_{\alpha\beta}(\omega) = - \int_{-\infty}^{\infty} dt \langle \langle r_{\alpha}(0); r'_{\beta}(t) \rangle \rangle e^{-i\omega t + \varepsilon t}. \quad (2.49)$$

Equation (2.49) relates the dynamic polarizability in the frequency domain to the propagator through a Fourier transform. This is generalized for any time-independent operator

$$\hat{A}(0) \quad (2.50)$$

and time-varying operator

$$\hat{B}(t) \quad (2.51)$$

in the interaction picture using the notation

$$\langle \langle \hat{A}; \hat{B} \rangle \rangle_{\omega + i\varepsilon} = \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^{\infty} dt \langle \langle \hat{A}(0); \hat{B}'(t) \rangle \rangle e^{-i\omega t + \varepsilon t}. \quad (2.52)$$

The Green's function will now be expressed over molecular states of the system, in order to facilitate its physical interpretation. To obtain a spectral representation of the polarization propagator, the resolution of the identity for the zeroth-order eigenstates is inserted into Eq (2.42)

$$\begin{aligned} \langle \langle \hat{A}(0); \hat{B}'(t) \rangle \rangle &= -i\Theta(-t) \sum_n \{ \langle k | \hat{A} | n \rangle \langle n | e^{iH_0 t} \hat{B} e^{-iH_0 t} | k \rangle \\ &\quad - \langle k | e^{iH_0 t} \hat{B} e^{-iH_0 t} | n \rangle \langle n | \hat{A} | k \rangle \}. \end{aligned} \quad (2.53)$$

Because the states $|n\rangle$ are eigenfunctions of H_0 , this may be written

$$\begin{aligned} \langle\langle \hat{A}(0); \hat{B}^\dagger(t) \rangle\rangle &= -i\Theta(-t) \sum_n \{ \langle k|\hat{A}|n\rangle \langle n|\hat{B}|k\rangle e^{i(E_n^{(0)} - E_k^{(0)})t} \\ &\quad - \langle k|\hat{B}|n\rangle \langle n|\hat{A}|k\rangle e^{-i(E_n^{(0)} - E_k^{(0)})t} \}. \end{aligned} \quad (2.54)$$

Inserting Eq (2.54) into Eq (2.52) and integrating yields

$$\langle\langle \hat{A}; \hat{B} \rangle\rangle_\omega = \lim_{\varepsilon \rightarrow 0^+} \sum_n \left\{ \frac{\langle k|\hat{A}|n\rangle \langle n|\hat{B}|k\rangle}{\omega - E_n^{(0)} + E_k^{(0)} + i\varepsilon} - \frac{\langle k|\hat{B}|n\rangle \langle n|\hat{A}|k\rangle}{\omega + E_n^{(0)} - E_k^{(0)} - i\varepsilon} \right\}. \quad (2.55)$$

The spectral representation of the electron propagator for non-number conserving operators $\hat{A}$ and $\hat{B}$ has the form of Eq (2.55), but contains a positive sign between terms of the right-hand side.

The TDA Representation of States

If the zeroth-order Hamiltonian is assumed to be the Fock operator, the Hartree-Fock ground state $|0\rangle$ can then be substituted as the reference function $|k\rangle$ in the perturbation sequence. The zeroth-order eigenstates which form the orthogonal complement of the manifold $\mathcal{N}$ can be represented most simply—considering the one-electron nature of the perturbing operators—by the set of determinants formed from the single replacement of an occupied molecular orbital with a virtual one. The second-quantized form of these determinants are obtained by projecting on the reference function $|0\rangle$ the set of excitation operators⁹

$$\begin{aligned} +^3Q_{ia}^\dagger &= a_\alpha^\dagger i_\beta \\ -^3Q_{ia}^\dagger &= a_\beta^\dagger i_\alpha \\ ^3Q_{ia}^\dagger &= \frac{1}{\sqrt{2}} [a_\alpha^\dagger i_\alpha - a_\beta^\dagger i_\beta] \end{aligned} \quad (2.56)$$

for triplet and

$$^1Q_{ia}^\dagger = \frac{1}{\sqrt{2}} [a_\alpha^\dagger i_\alpha + a_\beta^\dagger i_\beta] \quad (2.57)$$

for the singlet excitations.

The virtual orbitals of the reference function $|0\rangle$ are formed from a Fock potential which leads to Koopmans' theorem, and therefore experience an incorrect interaction potential. The single replacement determinants constructed using these orbitals are hence not the optimal representation for excited states. An improved form for an excited state function can be constructed as a linear combination of the single replacement determinants

$$\begin{aligned} q_n^\dagger &= \sum_{ia} Q_{ia}^\dagger Z_{ia}^n \\ q_n &= \sum_{ia} Z_{ia}^{*n} Q_{ia} . \end{aligned} \quad (2.58)$$

The Hermitian conjugate of the excitation operator is introduced in Eq (2.70). The excitation operators are annotated by the super index ia , which labels the particle-hole space of the system. The representation of states by the creation operators in Eq (2.58) is referred to as the Tamm-Dancoff Approximation (TDA)⁵¹.

The state energies and the coefficients of expansion of the single replacement determinants can be variationally obtained by solving

$$E_n \leq \frac{\langle q_n | H | q_n \rangle}{\langle q_n | q_n \rangle} \quad (2.59)$$

which, using the definitions in Eq (2.58), is expressed as an eigenvalue problem in the matrix form

$$\mathbf{Z}^\dagger \left(\mathbf{Q}^\dagger | H | \mathbf{Q} \right) \mathbf{Z} = \mathbf{Z}^\dagger \left(\mathbf{Q}^\dagger | \mathbf{Q} \right) \mathbf{Z} \mathbf{E} . \quad (2.60)$$

Equation (2.60) is written in superoperator notation. The matrix $\mathbf{A}$ is introduced as shorthand notation of the TDA energy

$$\mathbf{A} = \left(\mathbf{Q}^\dagger | H | \mathbf{Q} \right) = \langle 0 | \left[\mathbf{Q}, H, \mathbf{Q}^\dagger \right] | 0 \rangle , \quad (2.61)$$

where the double commutator defined by

$$[\mathbf{Q}, H, \mathbf{Q}^\dagger] = \frac{1}{2} \{ [\mathbf{Q}, [H, \mathbf{Q}^\dagger]] + [[\mathbf{Q}, H], \mathbf{Q}^\dagger] \} , \quad (2.62)$$

and the second-quantized Hamiltonian is given in Eq (1.23). The TDA superoperator metric for a Hartree-Fock reference is

$$(\mathbf{Q}^\dagger|\mathbf{Q}^\dagger) = \langle 0|[\mathbf{Q}, \mathbf{Q}^\dagger]|0\rangle = 1. \quad (2.63)$$

The matrix elements of $\mathbf{A}$ are determined over spin-orbitals by evaluating the commutators in Eq (2.61)

$${}^3\mathbf{A}_{ia,jb} = (\epsilon_i - \epsilon_a) \delta_{ij} \delta_{ab} - \langle aj||bi \rangle \quad (2.64)$$

$${}^1\mathbf{A}_{ia,jb} = (\epsilon_i - \epsilon_a) \delta_{ij} \delta_{ab} - \langle aj||bi \rangle. \quad (2.65)$$

The matrix $\mathbf{A}$ is of dimension M , the size of the particle-hole space, which is $O(N^2)$. Since the matrix $\mathbf{A}$ is Hermitian, its diagonalization is carried out through a unitary transformation. The unitary properties of the coefficients fulfill the following orthonormality and closure relations

$$\begin{aligned} \sum_{ia} Z_{ia}^{*n} Z_{ia}^m &= \delta_{mn} \\ \sum_n Z_{ia}^{*n} Z_{jb}^n &= \delta_{ij} \delta_{ab}. \end{aligned} \quad (2.66)$$

The form of the TDA matrix has a simple interpretation. The energy of a general HF orbital is obtained from Eq (1.43) as

$$\epsilon_p = \langle p|h|p \rangle + \sum_i^N \langle pi||pi \rangle. \quad (2.67)$$

The actual energy of the HF single determinant is not a simple sum of the HF occupied orbital energies, but compensates the sum so that the electron interaction terms are counted only once

$$E_{HF} = \sum_i^N \epsilon_i - \sum_{i<j}^N \langle ij||ij \rangle. \quad (2.68)$$

According to the form in Eq (2.65), each row (or column) of ${}^1\mathbf{A}$ can be interpreted as the interaction— scaled relative to the HF reference— of the single replacement determinants across the N-particle Hamiltonian. The diagonal elements of ${}^1\mathbf{A}$ have the value

$${}^1A_{ia,ia} = \epsilon_a - \epsilon_i - \langle ai||ai \rangle . \quad (2.69)$$

This is the exact expression for the single determinantal HF form of an excited state. In reference to Eq (2.69), the total energy for the ia 'th excited determinant properly removes all contributions from hole orbital i , includes the necessary one- and two-electron integrals for particle orbital a , and compensates for the fact that the Fock potential used to construct orbital a incorrectly reflects an interaction with an electron occupying i . Upon the diagonalization of the matrix $\mathbf{A}$, the single determinantal excited state *configurations* are allowed to *interact*, through the off-diagonal matrix elements.

The TDA formalism is hence equivalent with the Singly-Excited Configuration Interaction (CIS) method. The procedure results in an approximate expansion of the exact N-particle representation of the excited state from the basis of N one-particle singly excited determinants. The mixing of configurations causes the relaxation of some states while others are destabilized, an effect which is particularly pronounced when the major component of two states are configurations of the same symmetry. Because the perturbations to be considered are one-electron in nature, single replacement determinants— or a linear combination of such— are the only states which will produce non-zero matrix elements with the HF reference.

The CIS excited state represents an improvement to the single replacement determinant. However, in a completely rigorous CI expansion the doubly- and triply- excited determinants would interact across the N-particle Hamiltonian with the TDA states, and these determinants in turn interact with all determinants which are within two excitation levels above and below them. Upon diagonalization of the matrix representing the full CI expansion, the coefficients of expansion of the single replacement determinants would

reflect the interaction with doubles and triples, and the coefficients for doubles and triples are likewise affected by all their respective possible interactions. The full CI coefficients would in this case be totally relaxed, and the wavefunctions constructed using them would then represents the exact N-particle solutions to the non-relativistic Born-Oppenheimer form of the Schrödinger equation, within the chosen basis⁵². Although an extremely simple process to visualize, the full CI expansion for even a modest-sized molecule is a monumental task in terms of computer storage and operations.

Because of the great computational effort required to obtain the full CI state representations, methods such as the INDO/S²⁶⁻²⁸ model Hamiltonian were specifically developed to parametrically account for the full relaxation of the reference and excited states using only a CIS calculation. For the application to properties of extended molecular systems, the INDO/S scheme will be employed to generate the HF reference function, with excited states represented by a particle-hole or augmented particle-hole scheme.

The RPA Representation of States

An alternative for the ground and excited state representations generated from a single determinantal reference is offered by the Random Phase Approximation (RPA)⁵³⁻⁵⁸. The RPA method is an extension of the TDA model, where the excitation operators used to project the TDA states from the reference $|0\rangle$ are supplemented by the set of de-excitation operators

$$\begin{aligned} {}^3_0Q_{ia} &= \frac{1}{\sqrt{2}} \left[i^\dagger_\alpha a_\alpha - i^\dagger_\beta a_\beta \right] \\ {}^1_0Q_{ia} &= \frac{1}{\sqrt{2}} \left[i^\dagger_\alpha a_\alpha + i^\dagger_\beta a_\beta \right] . \end{aligned} \quad (2.70)$$

The matrix equation of the RPA energy, to be compared with that for TDA in Eq (2.60), is of dimension $2M$

$$\begin{bmatrix} (Q^\dagger|H|Q^\dagger) & (Q^\dagger|H|Q) \\ (Q|H|Q^\dagger) & (Q|H|Q) \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \begin{bmatrix} (Q^\dagger|Q^\dagger) & (Q^\dagger|Q) \\ (Q|Q^\dagger) & (Q|Q) \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} E . \quad (2.71)$$

The eigenvector matrix has the dimension $2M \times M$. The superoperator matrices are written in the shorthand notation

$$(\mathbf{Q}^\dagger | \mathbf{H} | \mathbf{Q}^\dagger) = (\mathbf{Q} | \mathbf{H} | \mathbf{Q})^* = \mathbf{A} \quad (2.72)$$

$$(\mathbf{Q}^\dagger | \mathbf{H} | \mathbf{Q}) = (\mathbf{Q} | \mathbf{H} | \mathbf{Q}^\dagger)^* = \mathbf{B}$$

with $\mathbf{A}$ defined in Eqs (2.64) and (2.65), and a general element of $\mathbf{B}$ being

$${}^1\mathbf{B}_{ia,jb} = \langle ib | a j \rangle \quad (2.73)$$

$${}^3\mathbf{B}_{ia,jb} = \langle ib | j a \rangle .$$

Upon the evaluation of the superoperator metric, Eq (2.71) becomes

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{bmatrix} E_n . \quad (2.74)$$

The eigenvalues and eigenvectors of the RPA method are then obtainable from the solution of a non-Hermitian matrix problem of dimension $2M$.

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B}^* & -\mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{bmatrix} = \begin{bmatrix} \mathbf{X}_n \\ \mathbf{Y}_n \end{bmatrix} E_n . \quad (2.75)$$

Alternatively, partitioning techniques have been developed which, through a series of transformations, reduce the RPA problem to the diagonalization of an Hermitian matrix of dimension M ^{8,59-61}. One way to accomplish this is to express Eq (2.75) in component form (for real $\mathbf{A}$ and $\mathbf{B}$)

$$\mathbf{A}\mathbf{X} + \mathbf{B}\mathbf{Y} = \mathbf{X}\mathbf{E}_{\text{RPA}} \quad (2.76)$$

$$\mathbf{B}\mathbf{X} + \mathbf{A}\mathbf{Y} = -\mathbf{Y}\mathbf{E}_{\text{RPA}} .$$

These equations may be added and subtracted, giving

$$(\mathbf{A} + \mathbf{B})(\mathbf{X} + \mathbf{Y}) = (\mathbf{X} - \mathbf{Y}) \mathbf{E}_{\text{RPA}} \quad (2.77)$$

$$(\mathbf{A} - \mathbf{B})(\mathbf{X} - \mathbf{Y}) = (\mathbf{X} + \mathbf{Y}) \mathbf{E}_{\text{RPA}} . \quad (2.78)$$

Equation (2.77) is then rearranged

$$(\mathbf{X} + \mathbf{Y}) = (\mathbf{A} + \mathbf{B})^{-1} (\mathbf{X} - \mathbf{Y}) \mathbf{E}_{\text{RPA}} \quad (2.79)$$

and inserted into Eq (2.78)

$$(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})(\mathbf{X} - \mathbf{Y}) = (\mathbf{X} - \mathbf{Y}) \mathbf{E}_{\text{RPA}}^2 . \quad (2.80)$$

The dimension of the problem has been halved, with the full spectrum of eigenvalues obtained as $\pm E_{\text{RPA}}$, but eigenvalue problem is yet non-Hermitian. This may be rectified by left-multiplication with $(\mathbf{A} - \mathbf{B})^{1/2}$

$$(\mathbf{A} - \mathbf{B})^{+1/2}(\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})^{+1/2}(\tilde{\mathbf{X}} - \tilde{\mathbf{Y}}) = (\tilde{\mathbf{X}} - \tilde{\mathbf{Y}}) \mathbf{E}_{\text{RPA}}^2 , \quad (2.81)$$

where the transformed vectors have been introduced

$$(\tilde{\mathbf{X}} - \tilde{\mathbf{Y}}) = (\mathbf{A} - \mathbf{B})^{+1/2}(\mathbf{X} - \mathbf{Y}) . \quad (2.82)$$

An analogous equation for the RPA eigenvalues involving the matrix $(\mathbf{A} - \mathbf{B})$ and the vectors

$$(\tilde{\mathbf{X}} + \tilde{\mathbf{Y}}) = (\mathbf{A} + \mathbf{B})^{+1/2}(\mathbf{X} + \mathbf{Y}) \quad (2.83)$$

can be formulated by a similar series of operations.

The above manipulations are dependent upon the existence of the matrices $(\mathbf{A} - \mathbf{B})^{1/2}$ and $(\mathbf{A} + \mathbf{B})^{+1/2}$, and therefore that the matrices $(\mathbf{A} - \mathbf{B})$ and $(\mathbf{A} + \mathbf{B})$ be positive definite. These are the stability conditions of the RPA eigenvalue problem^{8,9}. In the first chapter, a unitary transformation was applied to the HF reference, resulting in an equation which at first-order determined the form of the Fock potential, and contained a second-order term that characterized the stationary point of the energy hyper-surface (see Eq (1.34)). The second-order energy expression of Eq (1.34) is equivalent to the RPA energy representation. Later in this chapter, the matrix $(\mathbf{A} - \mathbf{B})$ will be related to RPA problems using real orbitals and Hermitian operators, such as those used in standard HF treatments. For the minimum HF configuration, all eigenvalues of the Hessian should be positive, which is equivalent to the statement that the RPA solution is stable. Often,

a closed-shell singlet HF minimum is obtained that is stable relative to the singlet form for $(A - B)$, but unstable towards the triplet form. This will be of some consequence in the evaluation of NMR spin-spin coupling parameters, which involve triplet excitation operators.

Since $(A + B)$ and $(A - B)$ are Hermitian, the matrix problem in Eq (2.81) can be diagonalized by a unitary transformation. This yields the canonical set of RPA eigenvalues, having the vectors

$$\begin{aligned} O_n^\dagger &= Q^\dagger X_n + Q Y_n \\ O_n &= X_n^\dagger Q + Y_n^\dagger Q^\dagger. \end{aligned} \quad (2.84)$$

Analogous to the superoperator metric for the creation operators $((Q^\dagger|Q^\dagger) = 1$ and $(Q|Q) = -1)$, the superoperator relations of the canonical RPA vectors

$$\begin{aligned} (O^\dagger|O^\dagger) &= 1 \\ (O|O) &= -1 \\ (O^\dagger|O) &= (O|O^\dagger) = 0 \end{aligned} \quad (2.85)$$

translate into the following orthonormality and closure relations

$$\begin{aligned} \sum_{ia} (Z_{ia}^{n*} Z_{ia}^m - Y_{ia}^{n*} Y_{ia}^m) &= \delta_{nm} \\ \sum_n (Z_{ia}^{n*} Y_{jb}^n - Y_{ia}^n Z_{jb}^{n*}) &= 0 \\ \sum_n (Z_{ia}^n Z_{jb}^{n*} - Y_{ia}^{n*} Y_{jb}^n) &= \delta_{ia} \delta_{jb}. \end{aligned} \quad (2.86)$$

The Representation of States for the Propagator

The theory of propagators was derived in Section 2.2 in a completely rigorous manner, but of course assumptions must be made with regard to the molecular Hamiltonian, and subsequently the form of the states of the system. To cast the propagator in

an equation which is computationally tractable, consider the real component for the propagator $\langle\langle[A, H]; B\rangle\rangle_\omega$, which from Eq (2.55) has the spectral representation

$$\begin{aligned} \langle\langle[A, H]; B\rangle\rangle_\omega = \sum_n \left\{ \frac{(E_n^{(0)} - E_k^{(0)}) \langle k|A|n\rangle \langle n|B|k\rangle}{\omega - (E_n^{(0)} - E_k^{(0)})} \right. \\ \left. - \frac{(E_k^{(0)} - E_n^{(0)}) \langle k|B|n\rangle \langle n|A|k\rangle}{\omega + (E_n^{(0)} - E_k^{(0)})} \right\}. \end{aligned} \quad (2.87)$$

Applying the identities $a(b-a)^{-1} = -1 + b(b-a)^{-1}$ and $a(b+a)^{-1} = 1 - b(b+a)^{-1}$, Eq (2.87) becomes

$$\begin{aligned} \langle\langle[A, H]; B\rangle\rangle_\omega = \sum_n \{ \langle k|B|n\rangle \langle n|A|k\rangle - \langle k|A|n\rangle \langle n|B|k\rangle \\ + \frac{\omega \langle k|A|n\rangle \langle n|B|k\rangle}{\omega - (E_n^{(0)} - E_k^{(0)})} - \frac{\omega \langle k|B|n\rangle \langle n|A|k\rangle}{\omega + (E_n^{(0)} - E_k^{(0)})} \}. \end{aligned} \quad (2.88)$$

Using the completeness of the zeroth-order states ($\sum_n |n\rangle \langle n| = 1$), the equation of motion for the propagator is derived

$$\omega \langle\langle A; B\rangle\rangle_\omega = \langle k|[A, B]|k\rangle + \langle\langle[A, H]; B\rangle\rangle_\omega. \quad (2.89)$$

Equation (2.89) can be written in a recursive fashion, defining the moment expansion of the propagator⁶²

$$\begin{aligned} \langle\langle A; B\rangle\rangle_\omega = \omega^{-1} \langle k|[A, B]|k\rangle \\ + \omega^{-2} \langle k|[[A, H], B]|k\rangle + \omega^{-3} \langle k|[[[A, H], H], B]|k\rangle + \dots \end{aligned} \quad (2.90)$$

Upon the introduction of superoperator algebra⁶³

$$\begin{aligned} \mathbf{H}\mathbf{A} &= [\mathbf{H}, \mathbf{A}] \\ \mathbf{1}\mathbf{A} &= \mathbf{A} \end{aligned} \quad (2.91)$$

and a power series expansion for the inverse operator

$$\omega^{-1} \sum_{i=0}^{\infty} \left(\frac{\mathbf{H}}{\omega} \right)^i = (\omega \mathbf{1} - \mathbf{H})^{-1} \quad (2.92)$$

the propagator is written using the superoperator resolvent

$$\langle\langle A; B\rangle\rangle_\omega = \left(A^\dagger | (\omega \mathbf{1} - \mathbf{H})^{-1} | B \right). \quad (2.93)$$

A basis of states is inserted in the moment expansion of the polarization propagator through the inner-projection technique^{64,65}

$$\langle\langle A; B \rangle\rangle_{\omega} = \left(A^{\dagger} | \tilde{\mathbf{h}} \right) \left(\mathbf{h} | \omega \mathbf{1} - \mathbf{H} | \tilde{\mathbf{h}} \right)^{-1} (\mathbf{h} | B) \quad (2.94)$$

where $\mathbf{h}$ is a column vector of the complete excitation operator manifold and $\tilde{\mathbf{h}}$ is the transposed row vector. For example, the RPA expression for the polarization propagator is obtained with the substitution $A=B=V$, by applying the operator manifold $\{Q^+, Q\}$ to the HF reference $|0\rangle$

$$\langle\langle V; V \rangle\rangle_{\omega} = \begin{bmatrix} (V|Q^{\dagger}) & (V|Q) \end{bmatrix} \begin{bmatrix} \omega \mathbf{1} + \mathbf{A} & \mathbf{B} \\ \mathbf{B} & -\omega \mathbf{1} + \mathbf{A} \end{bmatrix}^{-1} \begin{bmatrix} (Q^{\dagger}|V) \\ (Q|V) \end{bmatrix}. \quad (2.95)$$

Since the frequency-dependence of the problem enters via a diagonal matrix added to the RPA energy, the transformations of Eqs (2.76)-(2.81) can also be used to bring this energy representation to canonical form

$$\langle\langle V; V \rangle\rangle_{\omega} = (V|O^{\dagger}) \begin{bmatrix} \omega \mathbf{1} + \epsilon_{RPA} & 0 \\ 0 & -\omega \mathbf{1} + \epsilon_{RPA} \end{bmatrix}^{-1} (O^{\dagger}|V). \quad (2.96)$$

Equation (2.96) is in the form of the spectral representation of the propagator

$$\text{Re}\langle\langle V; V \rangle\rangle_{\omega} = \sum_n \left\{ \frac{(V|O_n^{\dagger})(O_n^{\dagger}|V)}{\epsilon_n + \omega} - \frac{(V|O_n^{\dagger})(O_n|V)}{\epsilon_n - \omega} \right\}, \quad (2.97)$$

which is interpreted to contain poles at the RPA state energy differences, with residues of the RPA transition moments.

It is not rigorously acceptable to define a TDA form for the propagator. The reason for this goes back to the equation of motion (Eq (2.89), which was derived with the requirement that the basis of states satisfy the off-diagonal hypervirial relation

$$\langle k | [A, H] | n \rangle = (E_n^{(0)} - E_k^{(0)}) \langle k | A | n \rangle. \quad (2.98)$$

For a single determinantal reference function using a particle-hole excitation scheme, RPA is the simplest method consistent with this criteria⁶⁶.

To demonstrate the relation of TDA and RPA to the hypervirial theorem, consider a ground state consisting of the HF single determinant corrected with double excitations

$$|k\rangle = N_0 \left(|0\rangle + \sum_{i<j, a<b} d_{ij}^{ab} Q_{ia}^\dagger Q_{jb}^\dagger |0\rangle \right) \quad (2.99)$$

and a single-replacement excited state representation

$$|n\rangle = \sum_{ia} c_{ia}^n Q_{ia}^\dagger |0\rangle. \quad (2.100)$$

A transition moment between the ground and excited states would then be

$$\langle k|A|n\rangle = N_0 \sum_{ia} c_{ia}^n \left\{ \langle 0|A Q_{ia}^\dagger |0\rangle + d_{ij}^{ab*} \langle 0|Q_{jb} Q_{ia} A Q_{ia}^\dagger |0\rangle \right\} \quad (2.101)$$

which using the definitions

$$\begin{aligned} X_{ia}^n &= N_0 c_{ia}^n \\ Y_{ia}^n &= N_0 \sum_{jb} d_{ia}^{jb*} c_{jb}^n \end{aligned} \quad (2.102)$$

leads to the following form of the hypervirial relation

$$\begin{aligned} & \sum_{ia} \left\{ \langle 0|[A, H] Q_{ia}^\dagger |0\rangle X_{ia}^n + \langle 0|Q_{ia} [A, H] |0\rangle Y_{ia}^n \right\} \\ &= E_{n0} \sum_{ia} \left\{ \langle 0|A Q_{ia}^\dagger |0\rangle X_{ia}^n + \langle 0|Q_{ia} A |0\rangle Y_{ia}^n \right\}. \end{aligned} \quad (2.103)$$

The resolution of the identity

$$1 = |0\rangle\langle 0| + \sum_{ia} Q_{ia}^\dagger |0\rangle\langle 0|Q_{ia} + \sum_{i<j, a<b} Q_{ia}^\dagger Q_{jb}^\dagger |0\rangle\langle 0|Q_{jb} Q_{ia} + \dots \quad (2.104)$$

is inserted in Eq (2.103). The functions $Q_{ia}^\dagger |0\rangle$ and $Q_{ia,jb}^\dagger |0\rangle$ represent all possible singly- and doubly-excited determinants, etc. Equation (2.104) is an exact relation within a complete HF basis, because the expansion of all possible excited determinants spans the complete N-electron space⁶⁷. Using the Brillouin condition and the one-electron nature of the operator A leads to

$$\begin{aligned} \langle 0|A H Q_{ia}^\dagger |0\rangle &= \sum_{jb} \langle 0|A Q_{jb}^\dagger |0\rangle \langle 0|Q_{jb} H Q_{ia}^\dagger |0\rangle \\ \langle 0|H A Q_{ia}^\dagger |0\rangle &= \langle 0|H |0\rangle \langle 0|A Q_{ia}^\dagger |0\rangle \\ &+ \sum_{jb} \langle 0|H Q_{ia}^\dagger Q_{jb}^\dagger |0\rangle \langle 0|Q_{jb} Q_{ia} A Q_{ia}^\dagger |0\rangle \end{aligned} \quad (2.105)$$

with analogous expressions for $\langle 0|Q_{ia}[A, H]|0\rangle$. Upon the identification that

$$A_{ia,jb} = \langle 0|Q_{jb}H Q_{ia}^\dagger|0\rangle - \langle 0|H|0\rangle \delta_{ij} \delta_{ab} \quad (2.106)$$

and

$$B_{ia,jb} = \langle 0|Q_{jb}Q_{ia}H|0\rangle \quad (2.107)$$

Eq (2.105) becomes

$$\begin{aligned} & \sum_{ia} [Z_{ia}^n \sum_{jb} \{ \langle 0|A Q_{jb}^\dagger|0\rangle A_{jb,ia} - \langle 0|Q_{jb}A|0\rangle B_{ia,jb}^* \} \\ & + Y_{ia}^n \sum_{jb} \{ -\langle 0|Q_{jb}A|0\rangle A_{ia,jb}^* + \langle 0|A Q_{jb}^\dagger|0\rangle B_{jb,ia} \}] \\ & = E_{\text{RPA}}^n \sum_{jb} [\langle 0|A Q_{jb}^\dagger|0\rangle Z_{jb}^n + \langle 0|Q_{jb}A|0\rangle Y_{jb}^n] . \end{aligned} \quad (2.108)$$

For an Hermitian operator A with real orbitals, the above reduces to the matrix form Eq (2.78), whereas for an anti-Hermitian operator, this reduces to Eq (2.77).

The RPA equations simultaneously satisfy the requirements of both the Hermitian and anti-Hermitian operators. In the TDA representation, the linear combination of single replacement functions are represented through the coefficients X , but the coefficients Y are zero. The TDA formalism is hence not properly balanced to satisfy the hypervirial theorem, and is not valid for the moment expansion of the equation of motion for the propagator. This shortcoming also precludes the equivalence of other TDA forms for quantum mechanical expressions. For instance, the hypervirial relation can be combined with the relation of the conjugate position and momentum variables of the exact wavefunction

$$[r, H] = i p \quad (2.109)$$

leading to the following forms for the dipole length, mixed, and dipole velocity forms of the static molecular polarizability

$$\begin{aligned} 2\alpha &= \sum_{n \neq 0} \frac{\langle 0|r|n\rangle \langle n|r|0\rangle}{E_n - E_0} = \\ & \sum_{n \neq 0} i \langle 0|r|n\rangle \langle n|p|0\rangle = \sum_{n \neq 0} \langle 0|p|n\rangle (E_n - E_0) \langle n|p|0\rangle . \end{aligned} \quad (2.110)$$

The coefficients $\mathbf{Y}$ contained in the RPA formalism symbolize the relaxation of the HF state relative to a product of single excitations. This enables the RPA method to satisfy the hypervirial relation, and also keeps the HF linear response state correct through first-order in electron correlation. However, a consistency problem exists with the canonical RPA excitation operators, since they do not obey a “killer” condition with the HF reference⁶⁸

$$\mathbf{O}_n|0\rangle = (\langle 0|\mathbf{O}_n^\dagger)^\dagger = \mathbf{Y}^\dagger \mathbf{Q}^\dagger|0\rangle \neq 0. \quad (2.111)$$

The $\mathbf{Y}$ coefficients are, in this sense, a measure of the error in using the HF single determinant as an approximation to the true RPA reference, because the exact RPA ground state would fulfill the relation

$$\mathbf{O}_n|\text{RPA}\rangle = (\langle \text{RPA}|\mathbf{O}_n^\dagger)^\dagger = 0. \quad (2.112)$$

It is bothersome to chemists in particular that the RPA formalism removes the simplified model of electrons occupying single-particle orbitals, but the representation of states is not what RPA is intended for. The RPA method is a theory for the response to external stimulation. The concept of an RPA “state” is not particularly necessary when investigating the result of a perturbation on a single determinantal reference.

DETAIL

The previous chapters introduced methods for the determination of the energy of molecular response, and models for the representation of molecular states through their electronic configurations. With the fundamental study of these techniques completed, the emphasis now turns to computational logistics. The following sections are concerned with the application of the theoretical tools in a manner which is computationally expedient, in keeping with the overall INDO strategy. Although the methods are specifically introduced for calculations using semiempirical wavefunctions, there will be no loss of generality in the development of the algorithms. The techniques are equally valid for use with *ab-initio* methods.

Using the TDA RSPT expressions, it is proven that the transformation to canonical states may be avoided if the HF representation of the energy is inverted. The inversion process results in the formation of the first-order TDA wavefunction, and this function is then used in an extremely efficient manner to extract the third-order TDA RSPT energy. The second-order RPA expression is then expressed in a form of the same dimension as the TDA equations, through a reduction of the frequency-dependent propagator equation. From this expression, the connection between RPA and Coupled-Perturbed HF is shown. An efficient algorithm is next presented to introduce the effect of matrix inversion through the solution of a set of linear equations. This is derived in a manner such that all contributions to the expansion of states over the full particle-hole space may be included. Finally, detailed expressions are given to avoid the transformation of the two-electron integrals to the molecular orbital basis. Performing the matrix inverse product in the semiempirical atomic orbital representation is found to improve the performance of the

algorithm dramatically, because of the truncated list of integrals retained in the ZDO approximation.

The TDA Expression of RSPT

The TDA method is, in concept, a very simple model for the representation of states under the influence of a one-electron perturbation

$$V = \sum_{p,q} \langle p|V|q \rangle p^\dagger q . \quad (3.1)$$

For the TDA RSPT expressions, the ground state $|k\rangle$ is approximated by the HF single determinant $|0\rangle$, and the orthogonal complement is constructed from a linear combination of all possible determinants having one virtual orbital replacing an occupied orbital

$$|n\rangle = q_n^\dagger |0\rangle = \sum_{ia} Q_{ia}^\dagger |0\rangle Z_{ia}^n , \quad (3.2)$$

with the coefficients of expansion chosen variationally as those which diagonalize the CIS matrix

$$\epsilon_{\text{TDA}} = Z^\dagger A Z . \quad (3.3)$$

The TDA transition moments between the ground and excited states are determined from the commutator of the second-quantized operators

$$\begin{aligned} \langle 0|V|n\rangle &= \langle V|q_n^\dagger\rangle = \langle 0|[V, q_n^\dagger]|0\rangle \\ &= \langle 0|Vq_n^\dagger|0\rangle = \sum_{ia} \langle 0|VQ_{ia}^\dagger|0\rangle Z_{ia}^n . \end{aligned} \quad (3.4)$$

The second line of Eq (3.4) follows from the killer condition of the canonical TDA states ($\langle 0|q_n^\dagger = 0$). Since the TDA energy representation is diagonal in the chosen basis, the matrix product for the sum-over-states form of the RSPT second-order equation can be concisely expressed

$$E_{TDA}^{(2)} = \sum_n \frac{(V|q_n^\dagger)(q_n^\dagger|V)}{\epsilon_n} = (V|q^\dagger) \epsilon_{\text{TDA}}^{-1} (q^\dagger|V) . \quad (3.5)$$

After the initial HF step, the evaluation of the second-order TDA RSPT energy involves

1. evaluating the property integrals of the perturbation over the atomic orbital functions, followed by their transformation to the molecular basis;
2. construction of the CIS matrix, which entails a change of basis of the two-electron interaction integrals from the atomic to the molecular set;
3. diagonalization of the CIS matrix, to obtain the canonical state energies and the coefficients of expansion for the single replacement determinants which are used to construct the TDA states;
4. a second transformation of basis for the property integrals, taking them from the molecular orbital space to the representation of transition integrals for the canonical TDA basis (Eq (3.4));
5. performing the TDA sum-over-states according to the matrix expression of Eq (3.5).

The above outline is sufficiently simple to implement, but is restricted with respect to the size of system which may be investigated. This is because of the geometric increase in the amount of computer Random Access Memory (RAM) which is required to accomplish the necessary operations. The TDA energy representation is of dimension M , which is determined by the number of occupied orbitals times the number of virtual orbitals for a given system. The TDA array size is then $M \times M$, which scales as roughly N^4 elements for a molecule represented by N orbitals.

In spite of the symmetry of the Hermitian TDA matrix, which may be exploited by retaining only the unique entries, the space needed for this type of post-HF calculation rapidly becomes prohibitive. For example, the benzene molecule (C_6H_6) has a minimum valence-only basis of 30 orbitals. The RAM needed to hold the lower-triangle of the

Fock matrix, assuming 32 bit wordlength, is 3.7 kilobytes. The same area for the TDA matrix of this system is approximately 200 kilobytes. For the 48 basis-function molecule naphthalene ($C_{10}H_8$), the Fock matrix occupies 9.4 kilobytes while the TDA matrix requires 1.3 *megabytes*.

The problem of storage is particularly illuminated when the space requisites for these matrices are compared to the RAM specifications of the average computer. As an example, the Digital Equipment Corporation VAX 11/780* possesses one megabyte of RAM, which must be shared by the data, the executable program, the operating system of the computer, and any other processes residing on the machine. The VAX and other computers utilize a virtual memory system, in which operations may be performed out of the physical boundaries of the main memory. This is achieved by paging the necessary storage locations into RAM when they are specifically required. The virtual computer memory only temporarily alleviates the space limitation problem, because a point is soon reached where a system Input/Output (I/O) for the paging process is required for nearly every floating point operation, and the computer thrashes between processes in an extremely inefficient manner. The standard diagonalization routines, which are used in the solution of the eigenvalue problem, can hence be expected to function optimally when the entire matrix is readily available in RAM for update during the diagonalization process.

It is feasible that an eigenvalue may be obtained for an array which is held entirely in external computer storage, by iterative projection techniques⁶⁹⁻⁷². Extension of this method beyond the first few roots is not always suggested, because as the eigenstates are projected from the energy representation, arbitrary roots of the matrix may inadvertently be omitted, particularly when degenerate states are encountered.

* The VAX computer system is admittedly past its heyday in computational chemistry. However, the immediate interest of this particular approach for the determination of molecular properties is for the practicing chemist, who is apt to use quantum chemical methods as a supplemental tool in research. It is more realistic to assume that only nominal computing power will be readily accessible to him or her on a routine basis and, for this reason, the VAX benchmark is deemed relevant.

It is of course possible to construct the TDA states by truncating the CI procedure to systematically include the specific number of single replacement determinants which can be efficiently accommodated. Since the state energy difference enters into the denominator of the RSPT expression, The CI functions closest in energy to the reference would be expected to contribute the largest terms to the sum-over-states. The dominant components of these low-lying states will be the single replacement determinants which are constructed by excitations from the occupied molecular orbitals of highest energy into the unoccupied orbitals of lowest energy. The logical truncation of configurations would then be expected to consist of the particle-hole states closest to the Fermi level, provided that rotational invariance is maintained by not splitting a degenerate pair of determinants.

Restricting the particle-hole space of the CI expansion is often sufficient in the determination of the vertical transition energy. However, this in no way justifies its validity for the RSPT sum-over-states, particularly if the determinants omitted are of a proper symmetry to interact with the reference across the perturbing operator. For example, consider the calculation of the Fermi contact interaction, which is a term contributing to the nuclear spin-spin coupling constant of Nuclear Magnetic Resonance (NMR). The contact interaction is related to the direct probability density for each electron at the sites of the coupling nuclei (See Chapter 5). Electrons in s-type atomic states will naturally be important for this term. In the calculation of proton NMR determined within the ZDO approximation, the contact interaction is the only contributing term to the coupling, and s-type atomic states will provide the only non-zero contributions to the contact integral. The s-states are normally the major contributors to σ -type molecular orbitals, and in turn to the single determinantal Σ states which contribute to the CI procedure. If high- or low-lying Σ states are inadvertently excluded in the truncated CI, important contributions to the Fermi contact interaction are omitted from the sum-over-states.

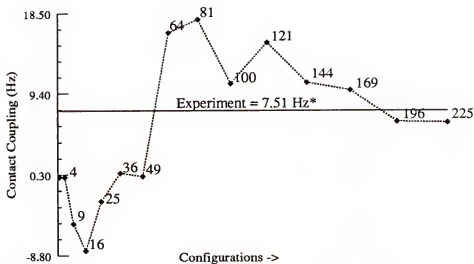


Figure I. The Fermi Contact Interaction of the Ortho Protons of Benzene (*Ref [73]).

This effect is graphically demonstrated in Figure I, which displays the Fermi contact coupling for two ortho protons of the benzene molecule plotted as a function of the number of singly-excited determinants included in the CI expansion. The contact calculations performed with limited representations including only the determinants closest in energy to the reference result in coupling values which are opposite in sign to experiment. This result contrasts the prediction that these functions alone will include the most significant contributions to a sum-over-states perturbative treatment of the property. In general, the CI sequence produces coupling values which vary dramatically, until most or all of the possible singly-excited determinants are included. Ultimately, the best TDA representation of states, particularly for the modelling of NMR spectroscopic parameters, will include the linear combination of all single replacement determinants. For extended systems, this will require an alternative to the matrix diagonalization method.

It will now be demonstrated that it is not absolutely necessary to depict the TDA states in canonical form for the evaluation of the sum-over-states energy expressions. The matrix diagonalization and the succeeding transformation of transition moments may be avoided by inversion of the HF representation of the TDA energy. Equation (3.5)

is first expressed in a form which includes the coefficients of expansion for the linear combination of single-replacement determinants

$$E_{TDA}^{(2)} = (\mathbf{V}|\mathbf{Q}^\dagger) \mathbf{Z} (\mathbf{Z}^\dagger \mathbf{A} \mathbf{Z})^{-1} \mathbf{Z}^\dagger (\mathbf{Q}^\dagger|\mathbf{V}) . \quad (3.6)$$

Since the expansion coefficients diagonalize an Hermitian matrix, the transformation is unitary

$$\begin{aligned} \mathbf{Z}^\dagger \mathbf{Z} &= \mathbf{Z} \mathbf{Z}^\dagger = \mathbf{1} \\ \mathbf{Z}^\dagger &= \mathbf{Z}^{-1} . \end{aligned} \quad (3.7)$$

The inverse of the TDA energy can therefore be written

$$\begin{aligned} \epsilon_{TDA}^{-1} &= (\mathbf{Z}^\dagger \mathbf{A} \mathbf{Z})^{-1} = \mathbf{Z}^{-1} \mathbf{A}^{-1} (\mathbf{Z}^\dagger)^{-1} \\ &= \mathbf{Z}^\dagger \mathbf{A}^{-1} \mathbf{Z} . \end{aligned} \quad (3.8)$$

Inserting Eqs (3.8) and using Eqs (3.7), the TDA second-order energy then becomes

$$\begin{aligned} E_{TDA}^{(2)} &= (\mathbf{V}|\mathbf{Q}^\dagger) \mathbf{Z} \mathbf{Z}^\dagger \mathbf{A}^{-1} \mathbf{Z} \mathbf{Z}^\dagger (\mathbf{Q}^\dagger|\mathbf{V}) \\ &= (\mathbf{V}|\mathbf{Q}^\dagger) \mathbf{A}^{-1} (\mathbf{Q}^\dagger|\mathbf{V}) . \end{aligned} \quad (3.9)$$

It would seem that the only thing gained by this is the elimination of a change of basis for the transition moments from the HF to the TDA representation, because the matrix diagonalization and inversion processes are both M^3 steps, and involve very similar algorithms. However, a technique will later be presented for an efficient alternative to the inversion of large matrices. The algorithm will be constructed such that the process may be performed at speeds approaching the time for an SCF calculation, making the investigation of large systems practical.

A TDA form of the resolvent operator is represented as

$$\mathcal{R}_{TDA} = |\mathbf{q}^\dagger\rangle \langle \mathbf{q}^\dagger| \mathbf{H} |\mathbf{q}^\dagger\rangle^{-1} \langle \mathbf{q}^\dagger| \quad (3.10)$$

and it may be used to form a first-order response function

$$|\Phi_{TDA}^{(1)}\rangle = \mathcal{R}_{TDA} \mathbf{V} |0\rangle = |\mathbf{q}^\dagger\rangle \langle \mathbf{q}^\dagger| \mathbf{H} |\mathbf{q}^\dagger\rangle^{-1} \langle \mathbf{q}^\dagger| \mathbf{V} \rangle . \quad (3.11)$$

The results of Eqs (3.7) and (3.8) allow for the expression of Eq (3.11) in its HF representation

$$|\Phi_{TDA}^{(1)}\rangle = |\mathbf{Q}^\dagger\rangle \mathbf{Z} \mathbf{Z}^\dagger \mathbf{A}^{-1} \mathbf{Z} \mathbf{Z}^\dagger (\mathbf{Q}^\dagger | \mathbf{V}) = |\mathbf{Q}^\dagger\rangle \mathbf{A}^{-1} (\mathbf{Q}^\dagger | \mathbf{V}) . \quad (3.12)$$

The function $|\Phi_{TDA}^{(1)}\rangle$ is used with Eq (2.28) to construct a sum-over-states form for the canonical TDA expression of the third-order energy

$$E_{TDA}^{(3)} = \sum_{m,n} (V | q_n^\dagger) (q_n^\dagger | H | q_n^\dagger)^{-1} (q_n^\dagger | V | q_m^\dagger) (q_m^\dagger | H | q_m^\dagger)^{-1} (q_m^\dagger | V) . \quad (3.13)$$

The canonical energy representations in Eq (3.13) are MxM diagonal matrices. For real functions, the excited state transition moments are contained in a symmetric or antisymmetric MxM matrix, depending on the Hermiticity of V, but the matrix is not diagonal in the canonical basis. This is manifested in the double sum over excited states in Eq (3.13).

The superoperator representation of the transition moments infers the antisymmetric character of the TDA excited states, as well as their normal product representation relative to the HF ground state

$$\begin{aligned} (q_n^\dagger | V | q_m^\dagger) &= \langle 0 | [q_n, V, q_m^\dagger] | 0 \rangle \\ &= \frac{1}{2} \left\{ \langle 0 | [q_n, [V, q_m^\dagger]] | 0 \rangle + \langle 0 | [[q_n, V^\dagger], q_m^\dagger] | 0 \rangle \right\} . \end{aligned} \quad (3.14)$$

Using the killer condition of the canonical TDA state creators ($q | 0 \rangle = 0$ and $\langle 0 | q^\dagger = 0$), the transition moments between excited states are determined to be

$$(q_n^\dagger | V | q_m^\dagger) = \langle 0 | q_n^\dagger V q_m^\dagger | 0 \rangle - \langle 0 | V | 0 \rangle \delta_{mn} . \quad (3.15)$$

Since the HF single determinant represents the TDA ground state, the TDA first-order RSPT energy is the HF expectation value of the perturbation

$$\langle 0 | V | 0 \rangle = E_{TDA}^{(1)} . \quad (3.16)$$

The following identity is recognized upon introducing the coefficients of expansion for the canonical TDA states

$$(q_a^\dagger | V | q_m^\dagger) = \sum_{ia,jb} Z_{ia}^{n*} \langle 0 | Q_{ia} (V - E_{TDA}^{(1)}) Q_{jb}^\dagger | 0 \rangle Z_{jb}^m . \quad (3.17)$$

As is anticipated from Eq (3.12), insertion of the coefficients of expansion for the TDA states into Eq (3.13) results in the elimination of the diagonalization-transformation steps, subject to an inverse HF energy representation

$$\begin{aligned} E_{TDA}^{(3)} &= (V | Q^\dagger) Z Z^\dagger A^{-1} Z Z^\dagger (Q^\dagger | V | Q^\dagger) Z Z^\dagger A^{-1} Z Z^\dagger (Q^\dagger | V) \\ &= (V | Q^\dagger) A^{-1} (Q^\dagger | V | Q^\dagger) A^{-1} (Q^\dagger | V) . \end{aligned} \quad (3.18)$$

An efficient recursive algorithm is used to expedite the evaluation of the above RSPT energies. The process is begun in the computation of $E_{TDA}^{(2)}$ with the solution of the inverse matrix problem

$$\Omega = A^{-1} (Q^\dagger | V) . \quad (3.19)$$

The particulars of the matrix inverse procedure will be detailed in a following section. The output of the procedure is the M-dimensional column Ω . The second-order RSPT energy at the TDA level is then obtained by a dot product of Ω with the M-dimensional row of transition integrals between the HF occupied and virtual orbitals

$$E_{TDA}^{(2)} = (V | Q^\dagger) \Omega . \quad (3.20)$$

The third-order RSPT expression in Eq (3.18) may also be written in terms of Ω

$$E_{TDA}^{(3)} = \Omega^\dagger (Q^\dagger | V | Q^\dagger) \Omega . \quad (3.21)$$

The first step in evaluation of the third-order energy is the formation of the M-dimensional column Υ

$$\Upsilon = (\mathbf{Q}^\dagger | \mathbf{V} | \mathbf{Q}^\dagger) \Omega . \quad (3.22)$$

Because the unitary transformations have been eliminated, the transition moment integrals between the TDA excited states need only be calculated at the HF-level

$$(\mathbf{Q}^\dagger | \mathbf{V} | \mathbf{Q}^\dagger)_{ia,jb} = \frac{1}{2} (\langle \phi_a | \mathbf{V} | \phi_b \rangle \delta_{ij} - \langle \phi_i | \mathbf{V} | \phi_j \rangle \delta_{ab}) . \quad (3.23)$$

The formation of the column Υ is accomplished efficiently by external storage of only the non-zero elements of the sparse transition moment matrix, with the matrix product processed directly as the integrals are brought into RAM. The overall cost of the procedure is M^2 , but is significantly less than this due to the manner in which the matrix product is carried out. The RSPT third-order energy is now obtained by a dot product with the row Ω

$$E_{TDA}^{(3)} = \Omega^\dagger \Upsilon . \quad (3.24)$$

The entire procedure is carried out at small additional computational expense to the second-order value.

The RPA Expression for the Propagator

Using the propagator formulation, the RPA version of the second-order energy expression may also be developed in a manner employing an inverse matrix relation of the HF representation. From this expression, it is then possible to show the equivalence of RPA to the Coupled-Perturbed HF equations. The RPA method at second-order hence give the linear response of the HF wavefunction, by virtue of its consistent treatment of the response through first-order in electron correlation.

The RPA expression of the frequency-dependent propagator was derived in Chapter Two

$$\langle\langle V; V \rangle\rangle_{\omega} = [(V|Q^{\dagger}), (V|Q)] \begin{bmatrix} \omega 1 + A & B \\ B & -\omega 1 + A \end{bmatrix}^{-1} \begin{bmatrix} (Q^{\dagger}|V) \\ (Q|V) \end{bmatrix}. \quad (3.25)$$

The propagator is expressed in the HF basis, and a frequency-dependent property over the chosen form for the perturbation V involves the inversion of a $2M \times 2M$ matrix for each value of ω . For the zero frequency ($\omega = 0$) case, the dimensionality of the problem can be reduced by half. This is accomplished by inserting unit matrices of the form⁹

$$\begin{aligned} U^{\dagger}U &= 1 \\ U &= \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & -1 \\ 1 & 1 \end{bmatrix} \end{aligned} \quad (3.26)$$

before and after the inverse energy representation. Equation (3.25) becomes

$$\begin{aligned} \langle\langle V; V \rangle\rangle_{\omega=0} &= \frac{1}{2} [(V|Q^{\dagger}) + (V|Q), (V|Q^{\dagger}) - (V|Q)] \\ &\times \begin{bmatrix} A + B & 0 \\ 0 & A - B \end{bmatrix}^{-1} \begin{bmatrix} (Q^{\dagger}|V) + (Q|V) \\ (Q^{\dagger}|V) - (Q|V) \end{bmatrix}. \end{aligned} \quad (3.27)$$

The transition moments over the second-quantized creation operators obey the identities

$$(V|Q) = -(V|Q^{\dagger}) \quad (3.28)$$

for Hermitian perturbations, and

$$(V|Q) = (V|Q^{\dagger}) \quad (3.29)$$

for anti-Hermitian cases. Inserting Eq (3.28) or (3.29) into Eq (3.27) leads to

$$\langle\langle V; V \rangle\rangle_{\omega} = 2 (V|Q^{\dagger}) (A - B)^{-1} (Q^{\dagger}|V) \quad (3.30)$$

for Hermitian V , and

$$\langle\langle V; V \rangle\rangle_{\omega=0} = 2 (V|Q^{\dagger}) (A + B)^{-1} (Q^{\dagger}|V) \quad (3.31)$$

in the anti-Hermitian situation. The above results agree with the contention of Chapter Two that the Hermitian perturbations involve the matrix $(\mathbf{A} - \mathbf{B})$ and the anti-Hermitian ones $(\mathbf{A} + \mathbf{B})$.

At this level, RPA theory is consistent with the linear response of the HF SCF wavefunction, and accordingly is the same result obtainable from the solution of the first-order Coupled-Perturbed HF (CPHF) equations⁷⁴⁻⁷⁷. This may be proven by comparison of the RPA formalism with the iterative equations for the CPHF coefficients. A general matrix element of the singlet $(\mathbf{A} - \mathbf{B})$ matrix is given as

$$(\mathbf{A} - \mathbf{B})_{ia,jb} = (\epsilon_i - \epsilon_a) \delta_{ij} \delta_{ab} + \langle ai || jb \rangle + \langle aj || ib \rangle. \quad (3.32)$$

If this is partitioned into a diagonal term ϵ , which contains only the orbital energy values, and a matrix $\mathbf{R}$ containing the remaining elements, the inverse of Eq (3.32) can be expressed in a power series

$$\begin{aligned} (\mathbf{A} - \mathbf{B})^{-1} &= \epsilon^{-1} (\mathbf{1} - \mathbf{R} \epsilon^{-1})^{-1} \\ &= \epsilon^{-1} + \epsilon^{-1} \mathbf{R} \epsilon^{-1} + \epsilon^{-1} \mathbf{R} \epsilon^{-1} \mathbf{R} \epsilon^{-1} + \dots \end{aligned} \quad (3.33)$$

Employing Eq (3.32), the matrix product

$$\Upsilon = (\mathbf{A} - \mathbf{B})^{-1} (\mathbf{V} | \mathbf{Q}) \quad (3.34)$$

can then be compared order-by-order as equivalent to the expansion of the first-order CPHF coefficients⁷⁸

$$\begin{aligned} \Upsilon_{ia} &= \frac{\langle i | V | a \rangle}{\epsilon_i - \epsilon_a} - \sum_{jb} \frac{(\langle ai || jb \rangle + \langle aj || ib \rangle) \langle j | V | b \rangle}{(\epsilon_i - \epsilon_a)(\epsilon_j - \epsilon_b)} \\ &+ \sum_{kjc} \frac{(\langle ck || ai \rangle + \langle ck || ia \rangle)(\langle bj || kc \rangle + \langle bj || ck \rangle) \langle j | V | b \rangle}{(\epsilon_i - \epsilon_a)(\epsilon_k - \epsilon_c)(\epsilon_j - \epsilon_b)} - \dots \end{aligned} \quad (3.35)$$

The Matrix Inverse Algorithm

It has been demonstrated for RSPT properties that the construction of canonical states and eigenvalues may be avoided through matrix inversion. In practice, it is not

necessary to actually calculate the inverse of the HF energy representation. Similar to the expression in Eq (3.34), the required inverse matrix is an element of a matrix product for an unknown M-dimensional column. This is described schematically as

$$\mathbf{X}^{-1}\mathbf{Y} = \mathbf{Z}, \quad (3.36)$$

where $\mathbf{X}$ is a symmetric matrix of dimension $M \times M$, and $\mathbf{Y}$ is a known $M \times 1$ column. The task of immediate interest is to determine the $M \times 1$ column $\mathbf{Z}$, which may be obtained by solving the system of linear equations

$$\mathbf{X} \mathbf{Z} = \mathbf{Y} \quad (3.37)$$

without knowledge of the actual inverse. Related procedures have been applied to many quantum chemical problems, such as the solution of the CPHF equations⁷⁹, determination of the amplitudes of the coupled-cluster equations⁸⁰, and accelerating the convergence of the SCF procedure⁸¹.

The solution for the column $\mathbf{Z}$ is approximated as a linear combination of columns

$$\mathbf{Z} = \sum_i \mathbf{z}_i \alpha_i \quad (3.38)$$

with the matrix product definition

$$\mathbf{X} \mathbf{z}_i = \beta_i \quad (3.39)$$

so that

$$\mathbf{X} \mathbf{Z} = \sum_i \beta_i \alpha_i. \quad (3.40)$$

By substituting Eq (3.40) into Eq (3.37), an expression for the variance of the approximate solution is obtained

$$\begin{aligned} \delta^2 &= (\mathbf{Y} - \sum_i \beta_i \alpha_i)^2 \\ &= \mathbf{Y}^\dagger \mathbf{Y} - 2 \sum_i \mathbf{Y}^\dagger \beta_i \alpha_i + \sum_{ij} \beta_i^\dagger \beta_j \alpha_i \alpha_j. \end{aligned} \quad (3.41)$$

Note that the matrix products of Eq (3.41) are scalar products, with the identity $\mathbf{Y}^\dagger \beta_i = \beta_i^\dagger \mathbf{Y}$. The variance is minimized with respect to the coefficients of expansion

$$\frac{d(\delta^2)}{d\alpha_k} = 0 = -2 \mathbf{Y}^\dagger \beta_k + 2 \sum_i \beta_k^\dagger \beta_i \alpha_i. \quad (3.42)$$

Using the definitions

$$\begin{aligned} \Theta_{ki} &= \beta_k^\dagger \beta_i \\ \Gamma_k &= \mathbf{Y}^\dagger \beta_k, \end{aligned} \quad (3.43)$$

the equation for α is written in matrix form

$$\Theta \alpha = \Gamma. \quad (3.44)$$

The coefficients are now determined from the relation

$$\alpha = \Theta^{-1} \Gamma. \quad (3.45)$$

It appears that one inversion problem has simply been replaced by another. However, the dimensionality of Eq (3.45) is that of the number of expansion columns, rather than of dimension M . The procedure is better illustrated by following a few iterations of the algorithm. The starting guess for the first expansion column is

$$(\mathbf{z}_1)_{ia} = \frac{\mathbf{Y}_{ia}}{\epsilon_i - \epsilon_a} \quad (3.46)$$

where ϵ_i is the HF orbital energy of ϕ_i . This choice is reasonable, considering the diagonal dominance and sparsity of the energy representations when the canonical HF molecular orbitals are employed. For calculations where localized orbitals are required, such as the RPA equations for the chemical shift of the NMR spectrum, it would prove expedient to perform the inverse product procedure prior to localization, because of the large off-diagonal elements which may be generated as an artifact of the localization⁸².

The first value β_1 is determined according to Eq (3.39), followed by the scalar products

$$\Gamma_1 = \mathbf{Y}^\dagger \beta_1 \quad (3.47)$$

$$\Theta_{11} = \beta_1^\dagger \beta_1 .$$

The first expansion coefficient is easily determined, and then the solution is compared to the actual column $\mathbf{Y}$ to obtain the residuum vector

$$\delta = \mathbf{Y} - \mathbf{z}_1 \alpha_1 . \quad (3.48)$$

If δ^2 is within a given tolerance, the procedure is halted. Otherwise, the residuum is used for the next guess vector in the basis of expansion columns. After determining β_2 , new elements of the matrices Γ and Θ are obtained

$$\Gamma_2 = \mathbf{Y}^\dagger \beta_2$$

$$\Theta_{12} = \Theta_{21} = \beta_1^\dagger \beta_2 \quad (3.49)$$

$$\Theta_{22} = \beta_2^\dagger \beta_2 .$$

The matrix inversion is now a symmetric 2x2, and the procedure is continued, with a new column added to the basis at each iteration until convergence.

For the benzene test case, which has a minimum basis valence-only particle-hole space of 225, the inverse matrix product requires 8 iterations to converge to an accuracy of 10^{-10} . The inverse matrix product of dimension 225x225 is thus converged in a subspace requiring the inversion of a matrix up to dimension 8x8.

All of the guess vectors and matrix products β_i are needed at each iteration, and are most conveniently stored externally and brought into RAM when required. The matrix product in Eq (3.39) is done for each guess vector, but this is also accomplished using external storage, as will be outlined in the proceeding section.

For the dynamic polarizability, the dimensionality of the problem is increased to 2M, and the inverse product must be performed for each frequency point. This introduces some minor modifications to the above procedure. The calculation is normally begun at

the static field ($\omega=0$) value. The first guess $\mathbf{z}_1^0$ is therefore the same as is used in Eq (3.45). The frequency-dependent expression of the inverse matrix product takes the form

$$\sum_i \begin{bmatrix} \omega + \mathbf{A} & \mathbf{B} \\ \mathbf{B} & -\omega + \mathbf{A} \end{bmatrix} \begin{bmatrix} \alpha_i^\omega z_i^\omega \\ \tilde{\alpha}_i^\omega \tilde{z}_i^\omega \end{bmatrix} = \sum_i \begin{bmatrix} \alpha_i^\omega \beta_i^\omega \\ \tilde{\alpha}_i^\omega \tilde{\beta}_i^\omega \end{bmatrix} \approx \begin{bmatrix} (\mathbf{Q}^\dagger | \mathbf{V}) \\ (\mathbf{Q} | \mathbf{V}) \end{bmatrix}. \quad (3.50)$$

The subsequent starting guess at each point is taken as the converged solution of the previous frequency

$$\begin{aligned} z_1^{\omega+\delta\omega} &= \sum_i z_i^\omega \alpha_i^\omega \\ \tilde{z}_1^{\omega+\delta\omega} &= \sum_i \tilde{z}_i^\omega \tilde{\alpha}_i^\omega. \end{aligned} \quad (3.51)$$

This is a particularly efficient starting choice when the increment ω is small. When approaching a pole of the propagator, the use of Eq (3.51) as the initial column can decrease the variance in the first iteration of the procedure by four orders of magnitude. As the sampled frequency ω increases, the matrix $(\omega + \mathbf{A})$ becomes increasingly diagonal-dominant, while the diagonal of the matrix $(-\omega + \mathbf{A})$ will contain an element which approaches zero. The convergence of the set of coefficients α is accordingly accelerated, while the coefficients $\tilde{\alpha}$ requiring additional cycles to converge.

The matrix product step to determine the β 's may be performed using four simultaneous matrix multiplications

$$\begin{aligned} \beta_i^\omega &= (\omega + \mathbf{A}) z_i^\omega + \mathbf{B} \tilde{z}_i^\omega \\ \tilde{\beta}_i^\omega &= \mathbf{B} z_i^\omega + (-\omega + \mathbf{A}) \tilde{z}_i^\omega. \end{aligned} \quad (3.52)$$

This simultaneous method is efficient because the same integrals are used as elements of the $\mathbf{A}$ and $\mathbf{B}$ matrices, so their processing can be best accomplished as one operation.

It is often stated that the individual expansion vectors $\mathbf{z}_i$ should be orthogonalized to increase numerical accuracy and speed the convergence of the inverse product. Using the procedure as outlined above, this does not appear to be the case, for test of the algorithm using orthogonal and nonorthogonal guess vectors invariably converged in the same number of iterations, with the orthogonal test case requiring additional computational

time, because of the added orthogonalization procedure. In conclusion, it should be mentioned that the inverse product, which has approximate dimension N^2 , is achieved with no more demand on RAM than the N -dimension HF SCF procedure.

Integral Processing

At each iteration of the matrix inverse product, multiplication of the energy representation with the guess vector is needed. The energy representation in the canonical HF basis is a large, sparse, diagonally dominant matrix. It is then most efficient to carry out the process in two steps

$$\beta_k = \xi_k + \zeta_k . \quad (3.53)$$

First, the guess vector is multiplied by the diagonal matrix of orbital energy differences

$$(\xi_k)_{ia} = (z_k)_{ia} (\epsilon_a - \epsilon_i) . \quad (3.54)$$

The diagonal matrix of orbital energy differences is used so often that it is best kept in RAM during the entire procedure. The product β_k is then completed by multiplication using the two-electron integrals which comprise the remainder of the matrix. This is represented symbolically by

$$(\zeta_k)_{ia} = \sum_{jb} \langle ia|jb \rangle (z_k)_{jb} . \quad (3.55)$$

Two of the molecular orbital integral labels target the element of z_k to multiply and the other two determine the location of the product ζ_k . This method for the matrix product avoids dimensioning of large matrices to handle the multiplication.

Equation (3.55) can be performed by processing the two-electron integrals in the atomic orbital basis. A similar technique is used in the solution of the CPHF equations⁸³. This is achieved by expanding the two-electron integrals of Eq (3.35)

$$(\zeta_k)_{ia} = \sum_{jb} \sum_{\mu\nu\sigma\lambda\delta\rho} c_\mu^i c_\nu^a c_\sigma^j c_\lambda^b \langle \mu\nu|\sigma\lambda \rangle \bullet z_{jb} , \quad (3.56)$$

with the notation c_μ^i introduced as the HF coefficient of atomic orbital μ for molecular orbital i . Equation (3.56) is regrouped as

$$(\zeta_k)_{ia} = \sum_{\mu\nu\sigma\lambda\delta\rho} c_\mu^i c_\nu^a \langle \mu\nu | \sigma\lambda \rangle \bullet Z_{\sigma\lambda} \quad (3.57)$$

using the definition

$$Z_{\sigma\lambda} = \sum_j c_\sigma^j \sum_b c_\lambda^b z_{jb} . \quad (3.58)$$

The product ζ_k is finally written

$$(\zeta_k)_{ia} = \sum_{\mu\nu} c_\mu^i c_\nu^a \tilde{Z}_{\mu\nu} . \quad (3.59)$$

The integrals which are utilized are now expressed in the atomic orbital basis

$$\tilde{Z}_{\mu\nu} = \sum_{\sigma\lambda} \langle \mu\nu | \sigma\lambda \rangle \bullet Z_{\sigma\lambda} . \quad (3.60)$$

The integral processing step in Eq (3.60) is performed by reading from external storage as many of the values as may be accommodated efficiently. The $\sigma\lambda$ indices of an integral determine the element of the lower triangular matrix $Z_{\sigma\lambda}$ to multiply, and the $\mu\nu$ indices target the location to which the product must be summed. The target matrix $\tilde{Z}_{\mu\nu}$ is symmetric for real singlet RPA (A-B), but requires computation of the full matrix in the triplet case, or when the perturbing operator is anti-Hermitian. The TDA version of $\tilde{Z}_{\mu\nu}$ is asymmetric in all cases.

There are two major advantages to performing the matrix product in this fashion. First, the atomic-to-molecular orbital transformation of the two-electron integrals, an inherent N^5 procedure, is avoided. Second, the atomic orbital two-electron integral list used in the semiempirical procedure is much shorter than the *ab-initio* list for the same number of orbitals. At the molecular orbital level, the two-electron integrals consist of all unique values having two occupied and two virtual indices. In the atomic basis,

the semiempirical integral list benefits from the ZDO restriction. The system time for retrieving the truncated semiempirical atomic orbital two-electron integral list is dramatically less than that associated with the list as expressed in the molecular orbital basis. This makes the atomic orbital procedure faster at each iteration of the matrix inverse product, in spite of the added steps in Eqs (3.58) and (3.59). As an example, Table I presents a comparison of execution time for the calculation of one component of the static field polarizability for ferrocene using the atomic versus the molecular two-electron integrals. It should not be surprising that the time of execution for the matrix inverse product is comparable to the HF SCF procedure, since they are both iterative atomic orbital integral driven processes.

Table I. Execution Time of the Polarizability Algorithm for Ferrocene (SCF Units).

Calculation	Transformation	Convergence	Total
MO basis	37.4	5.36	42.7
AO basis		1.55	1.55

APPLICATION: ELECTRIC FIELD RESPONSE

Calculations of electric field properties based on the techniques developed previously are now presented. Static electric field moments for a molecule are defined from the Taylor series expansion of the energy for the system. The values of the first molecular polarizability are given for various test cases, and are compared with experiment. The effect of p-type polarization functions added to the basis set of the hydrogen atoms is discussed. The results of isotropic coupling are found to be very satisfactory for the TDA method, however the anisotropy is poorly represented. It is demonstrated for benzene that this is not necessarily an artifact of the poor basis set description for the molecule in the direction parallel to the principal molecular axis. Examples are given which suggest the linearity of polarizability with the size of the molecule. Molecular hyperpolarizability is related to the third-order energy of RSPT. Calculated INDO/S TDA values are compared to other methods, and the effect of polarization functions is discussed. The INDO/S dynamic molecular polarizability is compared with *ab initio* results. The completeness of the ZDO basis is then investigated by calculations in the dipole length and velocity formulations, using the ZDO approximation as well as with the inclusion of two-center integrals.

Electric Field Properties

The use of the electric field as a quantum mechanical probe is well documented^{50,84-86}. This is attributable to its relative simplicity and availability relative to other possible avenues for the examination of molecular properties. A host of physical phenomena are

associated with this perturbation, including polarizability, second harmonic generation, optical rectification, and refractive index⁵⁰.

Upon exposing a molecule to an electric field, a dipole moment is induced in the system. Provided that the field strength $\mathbf{E}$ at the site of the molecule is not too large, the dipole moment relative to a particular Cartesian direction may be expanded in a power series

$$\mu_i = \mu_{0i} + \bar{\alpha}\mathbf{E}_i + \frac{1}{2!}\bar{\beta}\mathbf{E}_i^2 + \dots, \quad (4.1)$$

where μ_{0i} is the permanent electric dipole moment along the coordinate i , and the values $\bar{\alpha}$, $\bar{\beta}$, $\bar{\gamma}$, ... are second-, third-, ... rank tensor quantities referred to as the polarizability, hyperpolarizability, ... These tensor quantities characterize the curvature of the induced moment with respect to field strength in the direction of the applied field as well along other coordinate axes. The energy for this system is given by

$$\mathcal{E} = - \int \boldsymbol{\mu} \bullet d\mathbf{E} \quad (4.2)$$

which, upon insertion of Eq (4.1) gives for the static electric field case

$$\mathcal{E} = \mathcal{E}_0 - \mu_{0i}\mathbf{E}_i - \dots - \frac{1}{2}\bar{\alpha}_{ii}\mathbf{E}_i^2 - \bar{\alpha}_{ij}\mathbf{E}_i\mathbf{E}_j - \dots - \frac{1}{6}\bar{\beta}_{iii}\mathbf{E}_i^3 - \frac{1}{2}\bar{\beta}_{iiij}\mathbf{E}_i^2\mathbf{E}_j - \dots. \quad (4.3)$$

In Eq (4.3), $\mathcal{E}_0$ represents the energy of the system in the absence of the field. The electric field moments are related to perturbation theory through comparison of Eq (4.3) to the order-by-order RSPT energy expressions.

The permanent dipole moment of a system is then calculated from the first-order RSPT expression

$$\mu_{0i} = -\langle k|\mathbf{r}_i|k \rangle, \quad (4.4)$$

which is the expectation value of the electric field operator over the reference function. To evaluate the electric dipole elements, the INDO/S valence-only basis set is represented

by the Slater-Type Orbital (STO)⁸⁷

$$\frac{[2\zeta]^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} [Y_l^m(\theta, \phi)]^2. \quad (4.5)$$

A particular hydrogenic atomic orbital function is obtained from Eq (4.5) according to the choice of spherical harmonic $Y_l^m(\theta, \phi)$ and exponential constant ζ . The exponential constants are determined from Slater's rules⁸⁷, with the exception of the value of 1.2 for hydrogen. Except where explicitly noted, the matrix elements over the STO basis functions are calculated within the ZDO approximation.

Reported in Table II are values of the dipole moment calculated using the INDO/S HF reference (Debye units) for a series of test molecules. The conjugated systems are reported using C-C, C-N, C-O, and C-H bond lengths of 1.400, 1.151, 1.1282, and 1.088 Å respectively. The smaller molecules are presented at their experimental geometries. The results, in most cases, are reasonably quantitative. The ability of the INDO/S model to predict higher-order electric field properties will rely on its representation of the dipole transition moments between molecular states.

Table II. INDO/S Dipole Moments (Debye units).

System	INDO/S	Experiment
CO	0.83	0.11 ^a
NH ₃	2.17	1.47 ^a
H ₂ O	2.17	1.85 ^a
SO ₂	1.45	1.59 ^b
CH ₃ F	1.59	1.85 ^c
H ₂ CO	2.77	2.34 ^d
Toluene	0.93	1.45 ^d
Aniline	1.62	1.53 ^d
Pyridine	2.22	2.20 ^d

^a) Ref [20] ^b) Ref [90] ^c) Ref [88] ^d) Ref [89]

Polarizability

Upon comparison to Eq (4.3), the molecular polarizability is determined from the second-order RSPT expression as

$$\alpha_{ij} = -2 \sum_{n \neq k} \frac{\langle k | \mathbf{r}_i | n \rangle \langle n | \mathbf{r}_j | k \rangle}{E_k - E_n}. \quad (4.6)$$

Equation (4.6) makes use of the fact that the dipole matrix elements are invariant to interchange of $\mathbf{r}_i$ and $\mathbf{r}_j$.

Table III presents values of the isotropic component of the static-field molecular polarizability

$$\alpha = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4.7)$$

which are evaluated within the RPA and TDA formalisms. From the results, it can be concluded that the TDA model consistently performs better than the RPA method. This should not be surprising, considering that the INDO/S model Hamiltonian is specifically parameterized to reproduce electronic spectra from the vertical transition energies obtained via a CIS calculation²⁸. The fact that the polarizability evaluated with TDA is always larger than its RPA counterpart may be rationalized according to the manner in which the respective states are constructed. Both methods employ an excited state description which is a linear combination of single replacement determinants, but the RPA technique includes specific relaxation of the ground state from a select set of singles products⁶⁶, which keeps the method correct through first-order in electron correlation. This relaxation of the reference function translates into an increase in the RPA vertical transition energy relative to the TDA value. Since this energy difference enters the denominator of the sum-over-states expression, it is reasonable to expect that the RPA calculations would produce lower values of the polarizability than TDA.

Table III also contains calculations which have been performed with both the minimal valence-only atomic orbital functions and the augmented basis which includes p-type

polarization functions added to the hydrogen centers. The exponential constant for the polarization functions is chosen as 1.0. The values obtained with the extended bases are invariably better in reproducing experimental result. The larger basis sets are more capable of accommodating charge migration, and hence are more reliable in predicting the polarizability.

Table III. The INDO/S Isotropic Molecular Polarizability ($\text{\AA}^3$).

System	TDA	RPA	Experiment
C_2H_4	1.80	1.64	4.22 ^a
C_2H_4^*	3.35	3.03	
H_2CO	1.24	1.06	2.45 ^a
H_2CO^*	2.11	1.84	
$\text{C}_6\text{H}_{12}(\text{chair})$	5.60	5.05	10.9 ^b
$\text{C}_6\text{H}_{12}(\text{chair})^*$	9.31	8.58	
Pyridine	7.47	6.11	9.5 ^a
Pyridine [*]	8.32	6.89	
Benzene	8.70	6.39	9.87 ^c
Benzene [*]	9.19	7.95	
Aniline	8.74	7.31	11.6 ^a
Aniline [*]	11.3	9.66	
Napthalene	14.1	11.7	16.5 ^c
Napthalene [*]	17.2	14.5	
Biphenyl	17.5	14.6	19.6 ^c
Biphenyl [*]	21.3	18.1	
Anthracene	21.4	17.7	25.4 ^c
Anthracene [*]	27.3	22.8	
Ferrocene(D5H)	15.6	12.4	19.3 ^d
Ferrocene(D5D)	14.8	12.8	
Ferrocene(D5D) [*]	16.0	14.0	

^a) ZDO basis augmented with polarization functions.

^a) Ref [91] ^b) Ref [92] ^c) Ref [93] ^d) Ref [94]

From a dimensional analysis of its fundamental units, the molecular polarizability is interpreted as an inherent volume effect, and the augmented bases are better able to span the molecular space. The spatial area of the minimal valence functions increases with the size of the system under investigation, and the extended basis accordingly contributes a lesser percentage of the polarizability in this case.

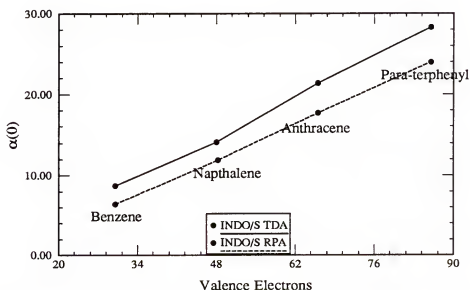


Figure II. The Isotropic Molecular Polarizability ($\text{\AA}^3$) of Benzene Derivatives.

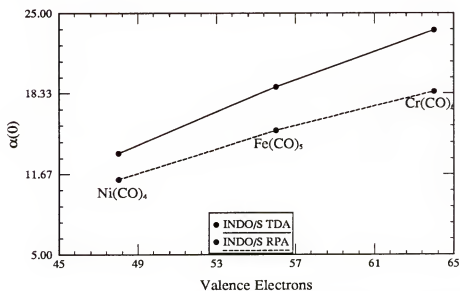


Figure III. The Isotropic Molecular Polarizability ($\text{\AA}^3$) for the Metal Carbonyl Series.

Empirical formulas have been presented which are based on the linear relation between the molecular polarizability and the size of the system⁹⁵⁻⁹⁸. This effect is graphically demonstrated in Figure II, which plots the isotropic polarizability for a series of benzene derivatives versus the number of valence electrons of the molecules. A similar plot is presented in Figure III for a series of metal carbonyl molecules.

Table IV. The Polarizability Components of Benzene and Ferrocene.

System		TDA	RPA	Experiment
Benzene	Perpendicular	12.4	8.90	11.0 ^a
	Parallel	1.40	1.37	6.9 ^a
Benzene*	Perpendicular	12.95	11.2	11.0
	Parallel	1.67	1.48	6.9
Ferrocene(D5D)	Perpendicular	13.7	11.7	15.9 ^b
	Parallel	15.6	13.8	19.3 ^b
Ferrocene(D5D)*	Perpendicular	14.3	12.2	15.9
	Parallel	19.4	17.6	19.3

*) ZDO basis set augmented with polarization functions.

^{a)} Ref [93] ^{b)} Ref [94]

Although the isotropic component of molecular polarizability is favorably reproduced with the INDO/S method, the anisotropy of the polarizability is incorrectly predicted. Table IV presents values of the polarizability parallel and perpendicular to the principal molecular axis as calculated for the benzene and ferrocene systems. The parallel polarizability is poorly represented, which may be attributed to the inadequate representation of the molecular basis in this direction. The effect of polarization functions is seen to overcompensate the predicted perpendicular component, rather than correct the anisotropy. For the ferrocene case, the d-type functions better balances the representation of basis.

Hyperpolarizability

From the Taylor Series expression of Eq (4.3), the expression which is quartic in electric field coordinate is equated to the RSPT hyperpolarizability, and is represented as

$$\beta_{ijk} = -\mathcal{P}_{IJK} \sum_{n,m \neq k} \frac{\langle k | \mathbf{r}_i | n \rangle \langle n | \mathbf{r}_j - \langle k | \mathbf{r}_j | k \rangle | m \rangle \langle m | \mathbf{r}_k | k \rangle}{(E_k - E_n)(E_k - E_m)}. \quad (4.8)$$

In Eq (4.8), the operator $\mathcal{P}_{IJK}$ indicates that all possible permutations of the Cartesian indices are to be included in the hyperpolarizability expression. The values will be reported in atomic units, but may be converted to SI units by the relation 1 a.u. = $3.20647 \times 10^{-53} \text{ C}^3 \text{m}^3 \text{J}^{-2}$.

Table V. The Non-Zero Components of Hyperpolarizability (a.u.) for CO and HF.

System	β_{zzz}	β_{xxz}		
	INDO/S TDA	Others	INDO/S TDA	Others
CO	23.27	22.79 ^a	-20.53	-19.80 ^a
		21.99 ^b		
HF	-18.16	-26.98 ^a	0.005567	6.019 ^a
	-19.54 [*]	-9.3 ^c		-0.4 ^c
		-8.4 ^d		0.0 ^d
		-11.0 ^e		-1.2 ^e
		-9.2 ^f		0.6 ^f

^a) ZDO basis set augmented with polarization functions.

^a) CNDO/2 (FF Ref [98]) ^b) *ab initio* FF (Ref [99]) ^c) *ab initio* FF A (Ref [100]) ^d) *ab initio* FF B (Ref [100]) ^e) MBPT(4) FF A (Ref [100]) ^f) MBPT(4) FF B (Ref [100])

Presented in Table V are INDO/S TDA hyperpolarizabilities for the CO (C-O 1.28212 Å) and HF (F-H 0.9170 Å) molecules. The atoms lie along the positive *z* axis, with the one listed first centered at the origin. The only non-zero components in this case are β_{zzz} and $\beta_{xxz} = \beta_{yyz}$. The INDO/S TDA hyperpolarizabilities for the CO molecule are

similar to the results obtained from CNDO/2 Finite-Field (FF) calculations⁹⁸. The β_{zzz} component agrees favorably with the *ab initio* FF results⁹⁹. The β_{xxz} are comparable for the semiempirical techniques.

For the HF molecule, the INDO/S TDA hyperpolarizabilities calculated using the valence only and polarization function bases are compared against the CNDO/S FF work⁹⁸, and *ab initio* FF calculations performed from the single determinant reference and SDQ MBPT(4) results using ((fluorinelhydrogen)) basis A: (6s5p3d15s3p) and basis B: (6s5p4d14s2p). For the INDO/S β_{zzz} component, the effects of polarization functions are not very dramatic. The β_{zzz} hyperpolarizability in the *ab initio* study decreases from basis A to B, however the basis augmentation is done for the fluorine atom in this case, at the expense of the hydrogen basis. The correlation of the reference function results in an increase in the predicted values. The β_{zzz} component of this system are predicted within the same order of magnitude by all the methods, and there exists some evidence from the INDO/S work and the *ab initio* study that the β_{xxz} component of this molecule is nearly zero.

Table VI. The Non-Zero Components of Hyperpolarizability (a.u.) for Ammonia.

Component	INDO/S TDA	Others
β_{zzz}	-2.048	-15.22 ^a
	-13.6*	-2.663 ^b
β_{yyz}	-12.46	-3.056 ^a
	-8.80*	-6.331 ^b
β_{yyy}	17.84	-1.528 ^a
	-8.40*	8.826 ^b
β	-16.18	-13.07 ^a
	-18.7*	-9.481 ^b

*^y) ZDO basis augmented with polarization functions.

^a) CNDO/2 FF (Ref [98]) ^b) *ab initio* CPHF (Ref [101])

Table VI contains the INDO/S TDA hyperpolarizabilities calculated for the ammonia molecule, using the N-H bond lengths 1.016 Å and H-N-H angle of 107°. For this C_{3v} system, the non-zero components are β_{zzz} , $\beta_{yyy} = -\beta_{yxx}$, and $\beta_{yyz} = \beta_{xxz}$. Also presented is the average hyperpolarizability, defined as

$$\beta = \frac{3}{5} (\beta_{zzz} + \beta_{yyz} + \beta_{xxz}) . \quad (4.9)$$

The INDO/S TDA and *ab initio* FF results are in general agreement, with the CNDO/2 FF calculation predicting a differing sign for the β_{yyy} tensor component. The calculations including polarization functions are of smaller magnitude, except for the β_{zzz} component.

The results of hyperpolarizability calculations for the water molecule are the subject of Table VII. The O-H bond distance used is 0.9580 Å, and the H-O-H bond angle is 104.2°. The orientation is $O^-H_2^+$ defined as a negative dipole moment. The non-zero tensor components of this C_{2v} molecule are β_{zzz} , β_{xxz} and β_{yyz} . The *ab initio* study is performed using FF from the HF reference and from an MBPT(4) reference¹⁰² using (oxygen|hydrogen) basis A: (6s4p2d|4s2p) and basis B: (6s5p4d|4s2p). The INDO/S TDA values agree quite well with the *ab initio* results, and are quite different with the CNDO/2 FF⁹⁸ calculation. The CNDO/2 FF value is opposite in its prediction of sign to the other works. The basis effect reduces the β_{xxz} component in the INDO/S TDA study, while increasing the other components.

Table VII. The Non-Zero Components of Hyperpolarizability (a.u.) for Water.

Component	INDO/S TDA	Others
β_{zzz}	11.86	39.73 ^a
	16.76*	8.1 ^b
		5.2 ^c
		11.5 ^d
		9.2 ^e
β_{xxz}	19.88	-47.78 ^a
	13.82*	12.9 ^b
		9.6 ^c
		14.3 ^d
		10.0 ^e
β_{yyz}	-0.07678	-38.42 ^a
	4.41*	0 ^b
		0.5 ^c
		1.9 ^d
		3.7 ^e

*^y) ZDO basis augmented with polarization functions.

^a) CNDO/2 FF (Ref [98]) ^b) *ab initio* FF A (Ref [102]) ^c) *ab initio* FF B (Ref [102])

^d) SDQ-MBPT(4) A (Ref [102]) ^e) SDQ-MBPT(4) B (Ref [102])

The hyperpolarizabilities of the fluorinated methane series are the subject of Table VIII and IX. The CH₄ and CF₄ molecules which are reported in Table VIII are assumed to be of T_d symmetry. The carbon atom is centered at the origin of the coordinate system, with bond angles of 109.47°, and C-H and C-F bond lengths of 1.094 and 1.317 Å, respectively. The only non-zero tensor component in this case is β_{xyz} . For methane, the INDO/S calculation including polarization functions in the basis of hydrogens results in a much smaller value of the hyperpolarizability, and places it in excellent agreement with the *ab initio* TDHF work.

Table VIII. The Hyperpolarizability (a.u.) for Methane and Tetrafluoromethane.

System	INDO/S TDA	Others
CH ₄	-22.07	-2.429 ^a
	-6.03 [*]	-6.495 ^b
CF ₄	12.48	1.341 ^a
		2.813 ^b

^{*}) ZDO basis augmented with polarization functions.

^a) CNDO/2 FF (Ref [98]) ^b) *ab initio* TDHF (Ref [105])

For the CH₃F, CH₂F₂ and CHF₃ results in Table IX, the *z* axis is chosen as the highest symmetry axis of a distorted tetrahedron, with the following distances for the C-H and C-F bonds (in Å)— CH₃F: 1.109 1.385, CH₂F₂: 1.093 1.360, CHF₃: 1.098 1.332. The effects of polarization functions included in the valence-only basis is very interesting in these cases. The minimal basis semiempirical calculations both predict the sign of the β_{zzz} tensor component of CH₂F₂ to be opposite that calculated in the *ab initio* TDHF calculation. However, the INDO/S TDA calculation of β_{zzz} which includes polarization functions is similar to the *ab initio* study in both sign and magnitude. The other components of hyperpolarizability in the polarization function-augmented calculation are also in good agreement for this system. The CNDO/S FF⁹⁸ method is also negative in sign for all remaining components. The average hyperpolarizability of the INDO/S TDA and the *ab initio* TDHF¹⁰⁵ results are in good agreement for this system.

For CH₃F and CHF₃ molecules, the CNDO/S FF results are again opposite in sign, with the valence-only INDO/S TDA predictions generally a factor of two that of the *ab initio* TDHF calculations. Except for the anomaly of the β_{zzz} component in the CH₃F molecule, the INDO/S TDA calculations including polarization functions are generally smaller in magnitude than their valence-only counterparts, and are generally in good

agreement with the *ab initio* work.

Table IX. Hyperpolarizabilities (a.u.) for the Mono-, Di- and Tri-Fluorinated Methanes.

	CH ₂ F ₂		CH ₃ F		CHF ₃	
	INDO/S	Others	INDO/S	Others	INDO/S	Others
β_{zzz}	-2.660	-3.774 ^a	31.04	-5.801 ^a	-42.19	6.892 ^a
	10.17 [*]	16.41 ^b	51.9 [*]	19.56 ^b	-19.62 [*]	-23.19 ^b
β_{yyz}	34.33	-5.395 ^a	19.43	-2.089 ^a	-3.370	2.370 ^a
	19.63 [*]	14.75 ^b	13.01 [*]	9.314 ^b	-2.321 [*]	-4.271 ^b
β_{xxz}	2.269	-4.054 ^a	19.43	-2.089 ^a	-3.370	2.370 ^a
	13.43 [*]	8.290 ^b	13.01 [*]	9.314 ^b	-2.321 [*]	-4.271 ^b
β_{xxx}	0.000	0.0000	-22.94	—	14.61	—
	0.000 [*]	0.0000	-7.13 [*]	-8.117 ^b	5.34 [*]	3.458 ^b
β	20.36	-7.921 ^a	41.95	-5.988 ^a	-29.79	6.986 ^a
	25.94 [*]	23.67 ^b	46.75 [*]	22.92 ^b	-14.56 [*]	-19.04 ^b

^{*}) ZDO basis augmented with polarization functions.

^a) CNDO/2 FF (Ref [98]) ^b) *ab initio* TDHF (Ref [105])

Dynamic Molecular Polarizability

Dynamic molecular polarizability is a measure of the linear response of a system to a periodic electric field. The propagator formalism has been previously introduced as a means to determine this property. The spectral form of the propagator

$$\langle\langle A; B \rangle\rangle_{\omega} = \lim_{\varepsilon \rightarrow 0} \sum_n \left\{ \frac{\langle k|A|n\rangle\langle n|B|k\rangle}{\omega - E_n + E_k + i\varepsilon} - \frac{\langle k|B|n\rangle\langle n|A|k\rangle}{\omega + E_n - E_k - i\varepsilon} \right\} \quad (4.10)$$

has a real component which expresses the sum-over-states form of the frequency-dependent polarizability¹⁰⁶ for the choice of operators $A = B = \mathbf{r}$

$$\alpha(\omega) = \Re\langle\langle \mathbf{r}; \mathbf{r} \rangle\rangle_{\omega} = 2 \sum_n \frac{\langle k|\mathbf{r}|n\rangle\langle n|\mathbf{r}|k\rangle (E_n - E_k)}{(E_n - E_k)^2 - \omega^2}. \quad (4.11)$$

Within the RPA approximation, the dynamic polarizability is obtained from the polarization propagator, expressed in the form¹⁰⁷

$$\alpha(\omega) = \langle\langle \mathbf{r}; \mathbf{r} \rangle\rangle_{\omega} = [(\mathbf{r}|\mathbf{Q}^{\dagger}), (\mathbf{r}|\mathbf{Q})] \begin{bmatrix} \omega\mathbf{1} + \mathbf{A} & \mathbf{B} \\ \mathbf{B} & -\omega\mathbf{1} + \mathbf{A} \end{bmatrix}^{-1} \begin{bmatrix} (\mathbf{Q}^{\dagger}|\mathbf{r}) \\ (\mathbf{Q}|\mathbf{r}) \end{bmatrix}. \quad (4.12)$$

The TDA formulation violates the off-diagonal hypervirial relation, and hence is not valid as a basis for the moment expansion of the propagator. Although the TDA method is invalid in a rigorous formulation of the propagator, a canonical state TDA expression of Eq (4.11) is possible

$$\alpha(\omega) = 2(\mathbf{r}|\mathbf{q}^{\dagger})(\epsilon_{\text{TDA}} + \omega\mathbf{1})^{-1}\epsilon_{\text{TDA}}(\epsilon_{\text{TDA}} - \omega\mathbf{1})^{-1}(\mathbf{q}^{\dagger}|\mathbf{r}). \quad (4.13)$$

Equation (4.13) presents an appealing computational advantage. Since the frequency matrix $\omega\mathbf{1}$ is a constant added to the diagonal of the TDA energy representation, it does not effect the unitary transformation which brings the states to canonical form. The physical interpretation of this is that the reference and TDA excited states are unperturbed by the sampled frequency. Once the canonical TDA states are constructed, it becomes a simple computational matter to utilize Eq (4.13) to obtain the TDA dynamic polarizability for a wide range of frequencies.

The canonical state TDA approach is again limited by the size of matrix which can be efficiently diagonalized, but this step is avoidable through the matrix inversion technique

$$\alpha(\omega) = (\mathbf{r}|\mathbf{Q}^{\dagger})(\mathbf{A} + \omega\mathbf{1})^{-1}\mathbf{A}(\mathbf{A} - \omega\mathbf{1})^{-1}(\mathbf{Q}^{\dagger}|\mathbf{r}). \quad (4.14)$$

It should be noted that Eq (4.14) can be manipulated into the form of Eq (4.12), if the matrix $\mathbf{B}$ is set equal to zero.

The parallel component of dynamic molecular polarizability from the RPA and TDA approaches is presented for the CO molecule in Figure IV. the calculation is performed at an internuclear separation of 1.128 Å. Also included in the figure are *ab initio* results

performed with a basis of 46 STOs. These calculations are performed using the RPA and the Second Order Polarization Propagator (SOPPA) approach¹⁰⁸. The SOPPA method is an RPA calculation which is consistent through second-order in electron correlation¹⁰⁹. As may be anticipated, the semiempirical basis does not have the flexibility to predict the polarizability component in the direction parallel to the principal axis of the molecule.

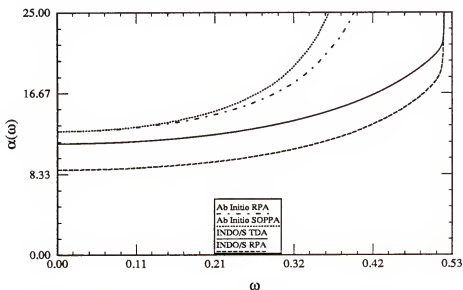


Figure IV. The Parallel Component of Dynamic Polarizability (a.u.) for CO.

Figure V graphs the perpendicular dynamic polarizability of CO in comparison with values obtained from *ab initio* RPA and SOPPA calculations¹⁰⁸. The dispersion of the semiempirical polarizability is comparable with the *ab initio* results through the first pole. However, the valence-only basis set leads to a limited representation of the second and higher poles of the system in comparison to the *ab initio* study.

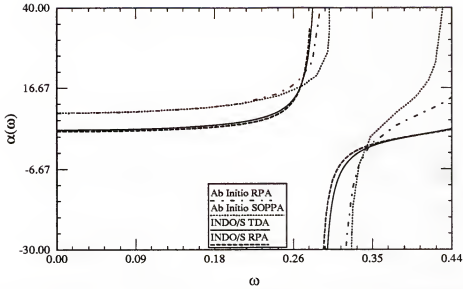


Figure V. The Perpendicular Component of Dynamic Polarizability (a.u.) for CO.

In Figure VI, the isotropic component of dynamic polarizability is plotted for the CH^+ ion, in comparison with *ab initio* RPA and SOPPA values⁴⁵. For this positively charged species, it is not necessary to employ an extensive basis to the description of the the diffuse Rydberg orbitals, and the 5 function INDO/S basis gives values of the dynamic polarizability which is similar to the 30 STO *ab initio* calculation through several poles.

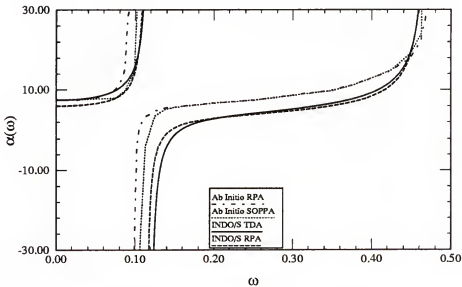


Figure VI. The Isotropic Dynamic Polarizability (a.u.) for CH^+ .

The parallel component of dynamic polarizability for the ferrocene system is graphed in Figure VII. This is intended as a demonstration of the method towards a system which is too extensive to be treated by more accurate methods. The semiempirical description for the anisotropy of the polarizability is reasonable for this system, and it is not overly optimistic to assume that the dynamic polarizability curve is more meaningful than an exercise of the computational method.

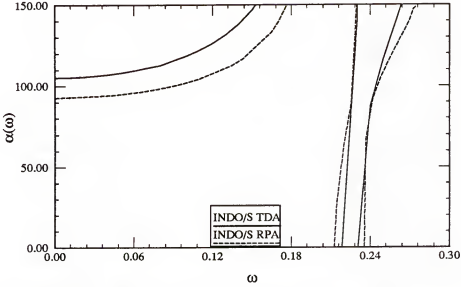


Figure VII. The Parallel Dynamic Polarizability (a.u.) for Ferrocene.

Using the off-diagonal hypervirial relation (Eq (2.98)) and Eq (2.109), an expression for the polarizability in the dipole velocity formulation may be obtained from Eq (4.11)

$$\alpha(\omega) = 2 \sum_n \frac{\langle k | \mathbf{p} | n \rangle \langle n | \mathbf{p} | k \rangle}{((E_n - E_k)^2 - \omega^2)(E_n - E_k)}. \quad (4.15)$$

The real component of the velocity form of the propagator $\langle \langle \mathbf{p}; \mathbf{p} \rangle \rangle_\omega$ has a spectral resolution of the form in Eq (4.10), with a substitution of $\mathbf{p}$ for $\mathbf{A}$ and $\mathbf{B}$, and hence cannot be directly cast into the form of Eq (4.15). Differentiating the velocity propagator leads to the following expression

$$\Re \frac{d \langle \langle \mathbf{p}; \mathbf{p} \rangle \rangle_\omega}{d\omega} = 4 \sum_n \frac{\omega \langle 0 | \mathbf{p} | n \rangle \langle n | \mathbf{p} | 0 \rangle (E_n - E_k)}{((E_n - E_k)^2 - \omega^2)^2}. \quad (4.16)$$

By expanding the denominator according to

$$\begin{aligned} & \left((E_n - E_k)^2 - \omega^2 \right)^{-2} = \\ & \left((E_n - E_k)^2 - \omega^2 \right)^{-1} (E_n - E_k)^{-2} \left(1 + \frac{\omega^2}{(E_n - E_k)^2} + \dots \right) \end{aligned} \quad (4.17)$$

the dynamic polarizability may be extracted from the velocity form of the propagator from the relation (for $\omega^2 \ll (E_n - E_k)^2$)

$$\alpha(\omega) = \Re \frac{1}{2\omega} \frac{d\langle \mathbf{p}; \mathbf{p} \rangle_\omega}{d\omega} . \quad (4.18)$$

Since the RPA method satisfies the off-diagonal hypervirial relation, calculations of the dynamic polarizability performed using the RPA formalism should be equal in both the length and velocity formalisms. Discrepancies between the velocity and length polarizability are then attributable to a deficiency of the basis set representation.

In order to further assess the impact of the ZDO approximation in relation to the basis set representation, calculations of the length and velocity dynamic polarizabilities were also performed where all two center integrals over STOs were retained in the expansion of transition moments. Recalling that the INDO SCF procedure is carried out under the assumption of a unit metric, the orthogonal coefficients of a semiempirical Roothaan equation are assumed to be related to the non-orthogonal set through the relation

$$\mathbf{C}' = \mathbf{S}^{1/2} \mathbf{C} . \quad (4.19)$$

The representation in both the orthogonal and non-orthogonal bases must be equivalent

$$\Phi \mathbf{C} = \Phi' \mathbf{C}' . \quad (4.20)$$

The nonorthogonal representation of the property integrals over STOs is therefore related to the orthogonal basis by a transformation involving the STO metric

$$\Phi' = \Phi \mathbf{S}^{-1/2} . \quad (4.21)$$

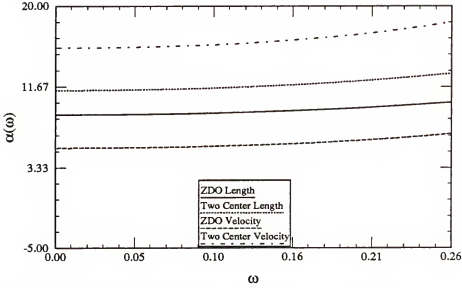


Figure VIII. The RPA Parallel Dynamic Polarizability (a.u.) for CO.

Figures VIII and IX compare the perpendicular and parallel components of dynamic polarizability for CO calculated in both the length and velocity formulations. Also reported are calculations performed with the retention of two center STO property integrals. The integrals are rotated to the orthogonal frame according to Eq (4.21). The agreement between the two calculations is not particularly good for either direction, but the disparity is particularly pronounced in the parallel direction. The length and velocity polarizabilities indicate that the ZDO approximation is justifiable in the basis set which contributes towards the perpendicular component, while reinforcing the contention that a deficiency exists in the functions representing the parallel direction.

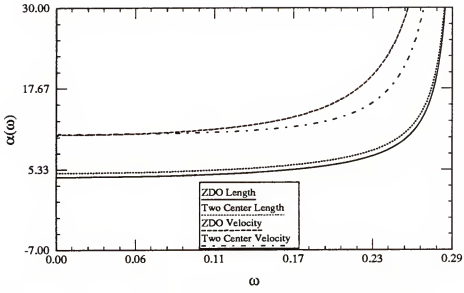


Figure IX. The RPA Perpendicular Dynamic Polarizability (a.u.) of CO.

APPLICATION: NUCLEAR SPIN-SPIN COUPLING

The INDO TDA and RPA techniques are now presented towards the determination of the nuclear spin-spin coupling constant. By treating the intramolecular coupling of nuclear spins as electron mediated, a second-order sum-over-states equation for the coupling constant is developed as a consequence of phenomenological Hamiltonian of the NMR experiment. A brief summary of the historical approaches taken in the calculation of coupling constants for semiempirical wavefunctions is then given. The finite field method and its application to the problem are discussed. Values of the coupling parameters between protons, ^{13}C coupling, and the $^{13}\text{C-H}$, and $^{13}\text{C-}^{19}\text{F}$ cases are calculated from the INDO TDA and RPA methods. It is found that the RPA couplings occasionally produce discrepancy in sign with the TDA couplings and with experiment. The finite field calculations of this coupling consequently suffer the same problem. In general, the TDA couplings predicted between protons and for $^{13}\text{C-H}$ are in excellent agreement with experiment.

Theory of Nuclear Spin-Spin Coupling

A nucleus of nonzero spin I_N possesses magnetic moment

$$\vec{\mu}_N = \gamma_N \vec{I}_N \quad (5.1)$$

where γ_N is the magnetogyric ratio of N . When this nucleus is placed in a magnetic field $\vec{H}_0$, a Zeeman splitting of the degenerate nuclear spin states occurs. For a field assumed along the z direction, the energy of the nuclear magnetic moment is given by

$$E_N = -\vec{\mu}_N \cdot \vec{H}_0 = -\gamma_N H_{0z} I_{Nz} , \quad (5.2)$$

where γ_N is the magnetogyric ratio for nucleus N. The eigenvalues of spin I_{Nz} are I, I-1, ..., -I. Electromagnetic radiation ν of the proper frequency creates the resonance condition by inducing transitions between the spin levels according the Bohr rule

$$2\pi\nu_N = \Delta E_N . \quad (5.3)$$

From the selection rule $|\Delta I_{Nz}| = 1$, the expression for the resonance condition is

$$\nu_N = \frac{\gamma_N H_0}{2\pi} . \quad (5.4)$$

The resonant frequency of a magnetic nucleus is proportional to the magnetic field which the nucleus experiences. In addition to $\vec{H}_0$, nuclei possessing magnetic moments create an intrinsic magnetic field. In a solid, this intermolecular dipole-dipole interaction can produce a dramatically enhanced local magnetic environment, causing the overlapping of individual resonances to form a broad absorption band. In nonviscous liquids the molecules are free to move randomly, which has the effect of averaging to zero this type of line broadening¹¹⁰, producing the high-resolution Nuclear Magnetic Resonance (NMR) spectra.

For a field applied along the laboratory z axis, the high-resolution spectra structure is represented by the phenomenological Hamiltonian (in Hertz)

$$\mathcal{H} = -H_0 \sum_N \gamma_N (1 - \sigma_N) I_{Nz} + 2\pi \sum_{N < M} J_{NM} \vec{I}_N \cdot \vec{I}_M . \quad (5.5)$$

The first term on the right-hand side of Eq (5.5) contains the screening constant or shielding parameter σ_N , which accounts for the fact that nuclei of the same species may experience differing local magnetic fields, due to their chemical environments. The second term describes the time-independent intramolecular interaction of nuclear spin moments. The physical description of this interaction is that the orientation of the magnetic moment of nucleus N influences the spin and magnetic moments of neighboring

electrons, which in turn affects the orientation of the moment of nucleus M. The value J_{NM} is the field-independent nuclear spin-spin coupling constant for centers N and M. The calculation of this value will be explored in the following text.

The intuition that the intrinsic interaction of nuclear spins is electron mediated allows the formulation of a tractable expression for the calculation of nuclear spin-spin coupling¹¹¹. The N-electron Hamiltonian is approximated as the usual sum of N one-electron Hamiltonians. The momentum of the electron corresponds to the classical description of a charged particle under the influence of the external and intrinsic magnetic field¹¹²

$$p^2 = \left(-i\vec{\nabla} + \frac{1}{2c}\vec{H}_0 \times \vec{r} + \frac{1}{c}\vec{A} \right)^2 . \quad (5.6)$$

In Eq (5,6), the magnetic field associated with the nuclear moment is described by the vector potential of a nuclear point dipole¹¹³

$$\vec{A}_N = \gamma_N \frac{\vec{I}_N \times \vec{r}}{r_N^3} = \vec{\nabla} \times \gamma_N \frac{\vec{I}_N}{r} . \quad (5.7)$$

In addition to the electron–nuclear attraction and electron–electron repulsion, the potential for interaction exists between the electron and the magnetic field. The force experienced between the intrinsic angular momentum of the electron and the dipolar magnetic field is expressed as

$$\vec{F} = \vec{\nabla} \left(\vec{S} \cdot \vec{H}_I \right) , \quad (5.8)$$

where the magnetic field $\vec{H}_I$ is generated from the curl of the point-dipole vector potential

$$\vec{H}_I = \vec{\nabla} \times \vec{\nabla} \times \gamma_N \frac{\vec{I}_N}{r} . \quad (5.9)$$

If the force in Eq (5.9) is interpreted according to Ehrenfest's theorem¹¹⁴, the potential energy is obtained as

$$V = -\vec{S} \cdot \vec{\nabla} \times \vec{\nabla} \times \frac{\vec{I}_N}{r} . \quad (5.10)$$

Application of the vector identity¹¹³

$$\vec{\nabla} \times \vec{\nabla} \times \vec{c} = \vec{\nabla} \left(\vec{\nabla} \cdot \vec{c} \right) - \nabla^2 \vec{c} \quad (5.11)$$

leads to two Hamiltonians for electron spin interaction with the nuclear point dipole. The first term in Eq (5.11) leads directly to the dipolar interaction between electron spin $\vec{S}_i$ and the nuclear spin moment $\vec{I}_N$ ¹¹³

$$H_{DP} = 2\beta \sum_N \gamma_N \sum_i \left[3 \left(\vec{S}_i \cdot \vec{r}_{iN} \right) \left(\vec{I}_N \cdot \vec{r}_{iN} \right) r_{iN}^{-5} - \left(\vec{S}_i \cdot \vec{I}_N \right) r_{iN}^{-3} \right] \quad (5.12)$$

where β is the collection of constants forming the Bohr magneton. Using the second term of Eq (5.11) and Gauss' theorem of surface integration¹¹⁵ yields the Fermi-contact interaction¹¹³

$$H_{FC} = \frac{16\pi\beta}{3} \sum_N \gamma_N \sum_i \delta(\vec{r}_{iN}) \vec{S}_i \cdot \vec{I}_N. \quad (5.13)$$

This term describes the interaction of an electron spin in direct contact— or, in wave-mechanical terms, the electron possessing non-zero probability density— at the site of the point nucleus.

For the calculation of nuclear spin-spin coupling, the connection is made between Eq (5.5) and perturbation theory¹¹¹. The total electronic Hamiltonian is partitioned in the usual way such that perturbing terms are those containing nuclear spin coordinates. The phenomenological expression of spin-spin coupling in Eq (5.5) contains the dot product of nuclear spin vectors, consequently terms of the perturbation sequence are sought which are second-order in nuclear spin. Similarly, equations for the shielding constant can be extracted, according to the first term of Eq (5.5), from the components of the perturbation sequence which are linear in H_{0z} and μ_z ^{111,116}.

From first-order RSPT, an energy contribution which is second-order in nuclear spin is obtained from the momentum term of the electron

$$E_{NM}^{(1)} = \frac{2}{3c^2} \gamma_N \gamma_M \langle k | \left(\vec{r}_N \times \vec{I}_N \cdot \vec{r}_M \times \vec{I}_M \right) r_N^{-3} r_M^{-3} | k \rangle. \quad (5.14)$$

Using the vector identity

$$(\vec{A} \times \vec{B}) \cdot (\vec{C} \times \vec{D}) = (\vec{A} \cdot \vec{C})(\vec{B} \cdot \vec{D}) - (\vec{A} \cdot \vec{D})(\vec{B} \cdot \vec{C}), \quad (5.15)$$

and the fact that the integration implied in Eq (5.14) is over the electronic coordinates, the first-order RSPT coupling expression which is of the phenomenological form is

$$J_{NM}^{(1)} = \frac{2}{3c^2} \gamma_N \gamma_M \langle k | (\vec{r}_N \cdot \vec{r}_M) r_N^{-3} r_M^{-3} | k \rangle. \quad (5.16)$$

The contributions to the coupling constant at second-order in electronic energy are terms of the type

$$E_{NM}^{(2)} = k_{NM}^{AB} \sum_{n \neq k} \frac{\langle k | \vec{A}_N \cdot \vec{I}_N | n \rangle \langle n | \vec{B}_M \cdot \vec{I}_M | k \rangle}{E_k - E_n}. \quad (5.17)$$

The nuclear spins are factored from the integration over electronic coordinates, which gives the coupling expression as a second-rank tensor

$$E_{NM}^{(2)} = k_{NM}^{AB} \sum_{n \neq k} \vec{I}_N \cdot \frac{\langle k | \vec{A}_N | n \rangle \langle n | \vec{B}_M | k \rangle}{E_k - E_n} \cdot \vec{I}_M. \quad (5.18)$$

The second-order electronic energy is in this case the coupling tensor for partially-ordered liquid crystals. For the random and rapid rotation of nonviscous liquid samples used in high resolution NMR experiments, $\mathbf{J}_{NM}$ may be replaced by the scalar quantity equal to one-third of its trace. The second-order RSPT expression for each component of the trace of the nuclear spin-spin coupling constant is obtained from the expression

$$2\pi J_{NM}^{AB} = \frac{2}{3} k_{NM}^{AB} \sum_{n \neq k} \frac{\langle k | \vec{A}_N | n \rangle \cdot \langle n | \vec{B}_M | k \rangle}{E_k - E_n} \quad (5.19)$$

where the factor of 2 arises from the presence of two equivalent terms in the perturbation sequence on the permutation of N and M. The techniques which have been developed to solve expressions of this type may now be applied to Eq (5.19) in order to determine the coupling parameters of the NMR spectrum.

The second-order RSPT expressions are obtained from the contact or dipolar Hamiltonian, along with a contribution from the orbital perturbation. This term is derived from the kinetic energy for an electron in motion in a magnetic field by using Eq (5.6)

$$H_N^{OB} = -2i\beta\gamma_N \vec{\mathbf{I}}_N \bullet \sum_i r_{iN}^{-3} \left(\vec{\mathbf{r}}_{iN} \times \vec{\nabla}_i \right) . \quad (5.20)$$

The triple scalar product identity is employed in order to arrange the orbital Hamiltonian into the phenomenological form of Eq (5.20)

$$\vec{\mathbf{A}} \bullet \vec{\mathbf{B}} \times \vec{\mathbf{C}} = -\vec{\mathbf{A}} \times \vec{\mathbf{B}} \bullet \vec{\mathbf{C}} . \quad (5.21)$$

The coupling constant for nuclei N and M is calculated from the six possible unique combinations of the orbital (OB), dipolar (DP), and contact (FC) operators substituted into Eq (5.19) for $\vec{\mathbf{A}}_N$ and $\vec{\mathbf{B}}_M$.

Much like the spin-orbit interaction, the contact and dipolar Hamiltonians contain spin and spatial coordinates which break the spin symmetry of the function on which they act. Consider, for example, the action of the contact operator

$$H_N^{FC} = \delta \left(\vec{\mathbf{r}}_1 - \vec{\mathbf{R}}_N \right) \vec{\mathbf{S}}_1 + \delta \left(\vec{\mathbf{r}}_2 - \vec{\mathbf{R}}_N \right) \vec{\mathbf{S}}_2 \quad (5.22)$$

on the two particle singlet determinantal wavefunction

$$\psi(1, 2) = \frac{1}{\sqrt{2}} \phi(1) \phi(2) [\alpha(1) \beta(2) - \alpha(2) \beta(1)] . \quad (5.23)$$

The S_z component is evaluated to be

$$\begin{aligned} H_N^{FC} \psi(1, 2) &= \frac{1}{\sqrt{2}} \phi(R_N) \phi(2) \left[\left(\frac{1}{2} \right) \alpha(1) \beta(2) - \left(-\frac{1}{2} \right) \alpha(2) \beta(1) \right] \\ &+ \frac{1}{\sqrt{2}} \phi(1) \phi(R_N) \left[\left(-\frac{1}{2} \right) \alpha(1) \beta(2) - \left(\frac{1}{2} \right) \alpha(2) \beta(1) \right] . \end{aligned} \quad (5.24)$$

Upon regrouping terms, the result of the operator is a function with the spin symmetry of the $M_s=0$ triplet

$$H_N^{FC} \psi(1, 2) = \frac{1}{2} \frac{1}{\sqrt{2}} [\phi(R_N) \phi(2) - \phi(1) \phi(R_N)] [\alpha(1) \beta(2) + \alpha(2) \beta(1)] . \quad (5.25)$$

This exercise demonstrates that the contact operator mixes singlet spin functions with functions of triplet symmetry. The DP Hamiltonian has a similar effect on the spin function of the state.

The OB term is specifically spin-independent, hence there are no cross-terms between the DP or FC with this operators. It is possible to formulate a cross-term containing the FC and DP contributions, but the individual operators have different angular dependence¹¹⁰. The diagonal elements of this tensor are zero, and will give no contribution to the isotropic coupling constant. However the off-diagonal elements of this tensor are the major contributions to anisotropic nuclear spin-spin coupling. The general expression for this term is given as

$$J_{NM}^{FC-DP} = \frac{32\beta^2}{9\pi} \sum_{n \neq k} \frac{\langle k | \delta(\vec{r}_N) \vec{S} | n \rangle \langle n | r_M^{-5} (\vec{S} \cdot \vec{r}_M) \vec{r}_M - r_M^{-3} \vec{S} | k \rangle}{E_k - E_n}. \quad (5.26)$$

The total second-order isotropic coupling expression hence reduces to the three contributions from individual products of the perturbing Hamiltonians.

If the electron spin vector is written in component form

$$\vec{S} = \vec{S}_x + \vec{S}_y + \vec{S}_z, \quad (5.27)$$

the cross-terms of the scalar product entering the second-order expression vanish, according to the rules of spin vector coupling¹¹⁷. The three parts of the scalar product due to $\vec{S}_x$, $\vec{S}_y$ and $\vec{S}_z$ contribute equally to the FC term. The spin vector may therefore be evaluated over the S_z component multiplied by a factor of 3. This leads to the following result for the FC coupling

$$J_{NM}^{FC} = -\frac{128\beta^2}{9} \gamma_N \gamma_M \sum_{n \neq k} \frac{\langle k | \delta(\vec{r}_N) |^3 n \rangle \langle^3 n | \delta(\vec{r}_M) | k \rangle}{^3 E_n - E_k}. \quad (5.28)$$

In Eq (5.28), the superscript to the state n indicates the spin symmetry of the excited state representation due to the action of the contact operator. The other non-zero second-order

contributions arise from the OB term

$$J_{NM}^{OB} = \frac{4\beta^2}{3\pi} \gamma_N \gamma_M \sum_{n \neq k} \frac{\langle k | r_N^{-3} (\vec{r}_N \times \vec{\nabla}) | n \rangle \bullet \langle n | r_M^{-3} (\vec{r}_M \times \vec{\nabla}) | k \rangle}{E_n - E_k} \quad (5.29)$$

and the DP component

$$J_{NM}^{DP} = -\frac{4\beta^2}{3\pi} \sum_{n \neq k} \frac{\langle k | 3r_N^{-5} (\vec{S} \bullet \vec{r}_N) \vec{r}_N - r_N^{-3} \vec{S} |^3 n \rangle \bullet \langle ^3 n | 3r_M^{-5} (\vec{S} \bullet \vec{r}_M) \vec{r}_M - r_M^{-3} \vec{S} | k \rangle}{^3 E_n - E_k} \quad (5.30)$$

Survey of Sum-Over-States Approaches to Coupling

Historically, the semiempirical evaluation of nuclear spin-spin coupling from the sum-over-states formulation has been improved through an increasing sophistication of the molecular state representations. The first perturbative studies of nuclear spin-spin coupling considered the interactions of nuclear spins solely through FC¹¹¹. The state energy differences in Eq (5.28) were approximated by employing one average excitation energy¹¹⁸. Under the assumption of a closed shell system, the first-order RSPT contact interaction energy is zero for a system of equal alpha and beta particles¹¹⁰, the n=k term is introduced into the sum in Eq (5.28). This allowed the resolution of the identity

$$\sum_{n \in \mathcal{N}} |n\rangle \langle n| = P_N + Q_N = 1_N \quad (5.31)$$

and a major simplification of the second-order expression

$$E_{NM}^{FC} = -\frac{128\beta^2}{9} \gamma_N \gamma_M ^3 \Delta E^{-1} \langle k | H_N^{FC} H_M^{FC} | k \rangle. \quad (5.32)$$

Second order calculations of nuclear spin-spin coupling from the Hückel and Extended-Hückel model Hamiltonians¹¹⁹ perform the sum over states in Eq (5.28) over an independent-particle wavefunction. The excited states $|n\rangle$ are constructed from the

reference function by a single replacement of occupied spin-orbital for one virtual spin-orbital, and the state energy difference between a particular excited state and the ground state in this case is the difference in energy between these two orbitals

$${}^3\Delta E = {}^1\Delta E = \epsilon_a - \epsilon_i . \quad (5.33)$$

When applied to HF SCF calculations, a denominator in the form of Eq (5.33) comprises the uncoupled Hartree-Fock method¹²⁰. Uncoupled HF is not consistent with an N-electron SCF procedure, where the virtual orbitals are constructed as being occupied by a psuedo-electron under the influence of the N-electron field. An inherent overcounting of coulomb and exchange terms occurs when the excited states are represented in this manner. To account for this discrepancy, the SCF theory of spin-spin coupling¹²¹ involves evaluating the matrix elements over determinantal states. Coupling calculations of this type¹²²⁻¹²⁴ employ denominators having the spin-orbital form

$$\begin{aligned} {}^3\Delta E &= \epsilon_a - \epsilon_i - \langle ia|ia \rangle \\ {}^1\Delta E &= \epsilon_a - \epsilon_i - \langle ia||ia \rangle . \end{aligned} \quad (5.34)$$

The sum-over-states equation using the denominators of the form in Eq (5.34) is known as the Nesbitt-Epstein perturbation theory¹⁰⁶.

The Nesbitt-Epstein shift may be construed as an approximate TDA calculation in which only the diagonal elements of the **A** matrix are retained

$$E_{NE}^{(2)} = k \sum_{ia} (V|Q_{ia}^\dagger) A_{ia,ia}^{-1} (Q_{ia}^\dagger|V) . \quad (5.35)$$

The diagonal inverse energy matrix has elements which represent the difference in energy between the HF reference determinant and the excited state determinant generated by a single replacement. However, this treatment neglects the coupling among excited states, represented by off-diagonal terms in this denominator matrix¹²⁵. In nuclear spin-spin coupling calculations, this leads to different coupling constants for equivalent pairs of

nuclei. For instance, calculations of the ^{19}F - ^{19}F coupling for different pairs of fluorines in tetra-fluoromethane vary between -113.1 and +12.1 Hz¹²⁶. Problems also arise if a localization procedure is desired to look at individual bond contributions to the coupling.

The problems with Nesbitt-Epstein sum over states procedures lead to developments allowing for the coupling of single replacement determinants by using triplet CIS for the FC and DP contributions, and singlet CIS for the OB term^{127,128}. The dramatic effect of truncation of the CI expansion on a coupling constant calculation was demonstrated in Chapter Three. In this presentation, the TDA matrix inverse algorithm is exploited to avoid the CPU time and RAM storage bottlenecks which limit the application of the CIS approaches.

The Finite Field Method

The most popular approach to the evaluation of semiempirical nuclear spin-spin coupling parameters is the finite field technique¹²⁹⁻¹³¹. In this method, the perturbing Hamiltonian is included directly in the SCF procedure

$$H(\lambda) = F + G + \lambda V. \quad (5.36)$$

The first-order energy is then given according to the Hellman-Feynman theorem^{132,133}

$$\begin{aligned} E^{(1)}(\lambda) &= \frac{dE(\lambda)}{d\lambda} = \\ &\left\langle \frac{d\Phi(\lambda)}{d\lambda} | H(\lambda) | \Phi(\lambda) \right\rangle + \left\langle \Phi(\lambda) | \frac{dH(\lambda)}{d\lambda} | \Phi(\lambda) \right\rangle + \left\langle \Phi(\lambda) | H(\lambda) | \frac{d\Phi(\lambda)}{d\lambda} \right\rangle \\ &= \left\langle \Phi(\lambda) | V | \Phi(\lambda) \right\rangle. \end{aligned} \quad (5.37)$$

The last identity in Eq (5.37) follows from the fact that the energy functional $|\Phi(\lambda)\rangle$ has variational parameters $c(\lambda)$ which are optimized in the presence of the perturbation, meaning that the functional is stationary in this degree of freedom¹³⁴

$$\frac{d\Phi(\lambda)}{d\lambda} = \frac{\partial\Phi(\lambda)}{\partial c(\lambda)} \frac{\partial c(\lambda)}{\partial \lambda} = 0. \quad (5.38)$$

In the example of an electric field perturbation¹³⁵⁻¹³⁷, this first-order energy would be the dipole moment induced by an applied molecular field (Eq (4.3)). For λ sufficiently close to zero the λ -induced dipole is linear, and the second and higher-order components of the Taylor Series expansion in Eq (4.3) are zero. The second-order energy can then be obtained as a difference derivative from the linear range of the induced dipole as follows

$$E^{(2)}(\lambda) = \frac{d^2 E(\lambda)}{d\lambda^2} = \frac{dE^{(1)}(\lambda)}{d\lambda} = \frac{E^{(1)}(\lambda) - E^{(1)}(0)}{\lambda} . \quad (5.39)$$

If the molecule does not possess a permanent dipole moment, the molecular polarizability may be obtained, for sufficiently small λ , as

$$\alpha = \frac{E^{(1)}(\lambda)}{\lambda} . \quad (5.40)$$

Semiempirical applications of the FF procedure for nuclear spin-spin coupling normally include only the Fermi-contact interaction. The one-electron portion of the Fock operator is in this case modified to include the perturbations of the two nuclear spin dipoles of interest

$$h' = h + \vec{H}'_N \bullet \vec{I}_N + \vec{H}'_M \bullet \vec{I}_M , \quad (5.41)$$

with the Hamiltonian $\vec{H}'_N$ representing the contact operator for nucleus N in Eq (5.13), which has the nuclear spin vector factored out. If rigorously treated, the coupling of centers N and M may be evaluated from the Hellman-Feynman theorem in the following manner

$$J_{NM}^{FC} = k_{MN} [\partial / \partial I_N \langle \Phi(I_N) | H_M | \Phi(I_N) \rangle]_{I_N=0} . \quad (5.42)$$

In actual practice, the expectation value for the operator H_M is calculated for the SCF wavefunction, and for a field-dependent SCF function at a small value of I_N , followed

by difference differentiation. The contact value is treated as a parameter whose value is obtained from a best fit to the experimental coupling data for a series of test molecules. These values are reported in Table X, along with those used in this study, and results from atomic SCF calculations.

This method has several attractive features. For a one-electron perturbation, the terms are simply added to the diagonal elements of the one-electron portion of the Fock matrix. It is thus easy to modify existing codes to accomplish this procedure. Since the orbitals and orbital energies obtained from the perturbed SCF are relaxed with respect to the perturbation, the wavefunctions constructed through any order in perturbative electron correlation will also obey the Hellmann-Feynman Theorem, and can be used in the above formulations. To perform a finite field calculation from a CI wavefunction, the procedure requires the CI Hamiltonian to include the perturbing term in order to insure that the configuration coefficients are relaxed in addition to the molecular orbital coefficients. This assures that all the variational coefficients obey Eq (5.38), and the Hellmann-Feynman Theorem holds.

A major detriment to the finite field method is the high numerical accuracy required in the calculation of induced moments. Numerical convergence to several decimal places is necessary to assure that the the difference derivative is valid, because the applied field strength λ must be sufficiently small such that the slope is linear in this region. Also, a minimum of two SCF's are required to perform the derivative along one coordinate. For evaluation of a third-order property, the numerical accuracy problem is further exacerbated. In addition, several derivatives of varying strength, each requiring an SCF calculation, need to be performed, and these derivatives themselves then must be numerically differentiated. Until recently, analytic techniques were considered too computationally demanding, and the difference derivative calculation was the only tractable approach to examine nonlinear properties. Recent developments, such as this

presentation, have reversed this situation.

The finite field energy is calculated as the linear response of the HF wavefunction. This energy may also be obtained analytically with the CPHF method, or—its equivalent—the RPA formalism. The finite field method hence is subject to instability problems. Examples of RPA couplings will be cited where the sign is calculated opposite to both that of the TDA results and to experiment. In each case, the values of FF couplings show a similar sign discrepancy.

All calculated values were performed using the INDO/1 model Hamiltonian which includes no interaction factors. This model consistently yielded better results than the INDO/S parameterization, particularly for the various proton couplings of aromatic molecules.

Proton Couplings

The valence-only ZDO basis of the semiempirical methods greatly simplifies the evaluation of nuclear spin coupling between protons, or for the coupling of protons with any other nuclei. For one reason, only one-center integrals are assumed to give non-zero contribution to the matrix elements over the perturbing Hamiltonians. In this case, only the orbitals associated with the coupling hydrogen nuclei enter into the matrix elements. In addition, the electronic distribution of the hydrogen atom is assumed to be represented by a single s-type function in the minimal valence-only semiempirical basis. The one-center s orbital integrals over the DP or OB term vanish in this case, because they each act as a ladder operator which in some way raises or lowers the angular or principal quantum number of the 1s function. The matrix element is then evaluated as a one-center overlap integral between functions of differing principal and/or angular quantum number, and thus is zero.

The Fermi contact interaction is hence the only contributing Hamiltonian to semiempirical coupling calculations involving protons. The TDA matrix element has a particularly simple form

$$(H_M^{FC} | q_n^\dagger) = \sum_{ia} c_{1s_M}^i c_{1s_M}^a \langle 1s_M | \delta(\vec{r} - \vec{R}_M) | 1s_M \rangle Z_{ia}^n. \quad (5.43)$$

The value of the contact integral which was employed in this study is obtained from the atomic wavefunction of Herman and Skillman¹³⁸. The integral over 1s functions may also be evaluated from Slater's rules⁸⁷ which, for the case of hydrogen is

$$\langle 1s_M | \delta(\mathbf{r}) | 1s_M \rangle = \frac{\zeta^3}{\pi}. \quad (5.44)$$

Table X. The Contact Integral Evaluated for First Row Atoms.

Atom	Herman-Skillman ^a	Slater's rules ^b	Atomic SCF ^c	Finite field ^d
H	0.550	0.5500	0.5500	0.3724
B	1.770	1.523	1.408	—
C	4.480	3.012	2.767	4.032
N	5.600	5.246	4.770	6.927
O	8.670	8.376	7.638	12.07
F	12.50	12.50	11.97	21.31

^a) Ref [138] ^b) Ref [87] ^c) Ref [139] ^d) Ref [130]

Table X presents the contact integral values for the first row atoms as calculated by Herman and Skillman, and from Slater's rules. Also included are a standard set of values calculated from SCF atomic wavefunctions¹³⁹. The results of the three are in reasonably agreement, with the exception of carbon. For comparison, the experimentally-parameterized values of the finite field method are also listed. These are seen to be quite different. For a good estimate of the proton coupling results which the FF method would

yield, the RPA results for the following test cases should be scaled by $(0.372/0.550)^2 = 0.457$.

Table XI. The Proton Coupling (Hertz) of Ethylene.

Geometry		^2J	$^3J(\text{trans})$	$^3J(\text{cis})$
H-C-H = 120.0	C-H = 1.334	9.87	21.9	6.95
	H-H = 1.087			
	C-H = 1.350	9.78	19.6	7.40
	H-H = 1.087			
	C-H = 1.334	10.35	20.6	7.76
	H-H = 1.100			
H-C-H = 115.0	C-H = 1.334	7.97	23.3	8.83
	H-H = 1.087			
	C-H = 1.350	8.00	22.7	6.85
	H-H = 1.087			
	C-H = 1.334	8.58	25.5	7.68
	H-H = 1.100			
	Experiment ^a	2.3	19.1	11.5

^a) taken from Ref [124]

It is of interest to first examine the geometry-dependence of the coupling constant. In Table XI, the calculated proton couplings of C_2H_4 are reported as a function of bond angle and bond distance. As would be expected, the geminal coupling is insensitive to change in C-C bond length, but a 2 picometer change in C-H bond distance effects the coupling by 1 Hertz. The same affect is achieved by varying the H-C-H bond angle by 5° . The cis- and trans- proton couplings are sensitive to bond angle distortion. Generally, the calculated coupling value is very geometry sensitive. This gives some indication as to why the NMR experiment is so important as a tool for determining molecular structure.

Proton couplings which are calculated from the INDO TDA and RPA methods are given in Table XII. For geminal hydrogens, the RPA is superior to the TDA approach. The numbering system of the benzene and naphthalene molecules are given in Figures X and XI, respectively. The benzene and naphthalene couplings are reproduced remarkably well by the TDA method in all cases.

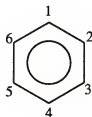


Figure X. The Numbering Scheme of Centers for Benzene.

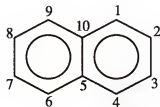


Figure XI. The Numbering Scheme of Centers for Napthalene

Table XII. TDA and RPA Proton Couplings (Hertz).

System	Coupling	TDA	RPA	Experiment
$^2J_{HH}$				
H ₂ O		-2.39	-14.4	-7.2 ^a
NH ₃		-1.65	-13.2	-10.4
CH ₄		-1.31	-9.34	-12.4
C ₂ H ₄		9.87	8.33	2.3
CH ₂ O		28.1	36.9	40.2
$^3J_{HH}$				
C ₂ H ₂		6.96	11.7	9.8 ^a
C ₂ H ₄ (trans)		21.9	37.1	19.1
C ₂ H ₄ (cis)		5.80	-11.1	11.5
Benzene				
	$^3J_{12}$	6.18	9.93	7.51 ^b
	$^4J_{13}$	2.51	3.41	1.33
	$^5J_{14}$	0.61	1.9	0.62
Naphthalene				
	$^3J_{12}$	9.61	15.5	8.3 ^b
	$^4J_{13}$	3.38	5.00	1.25
	$^5J_{14}$	0.763	2.26	0.00
	$^7J_{16}$	1.85	3.85	0.83
	$^6J_7$	-0.011	-0.360	-0.16
	$^5J_{18}$	0.150	0.563	0.21
	$^3J_{23}$	8.16	12.9	6.60
	$^7J_{27}$	0.047	0.388	0.280

^{a)} taken from Ref [124] ^{b)} taken from Ref [73]

Table XIII presents the couplings between protons and ^{13}C for various systems. The TDA couplings agree extremely well with experimental result. Neither the RPA values or the values scaled to FF calculations reproduce experiment as well, and in several cases predict a difference in sign.

Table XIII. ^{13}C -H Couplings (Hertz) for Various Systems.

System	Coupling	TDA	RPA	Experiment ^a
$^1J_{\text{CH}}$				
CH_4		121.4	169.3	125.0
C_2H_2		269.3	341.0	249
C_2H_4		161.2	221.5	156.2
CH_3F		141.7	199.0	149.1
CH_2F_2		203.6	287.3	184.5
CHF_3		220.7	300.0	239.1
CH_2O		186.2	264.7	172.0
$^2J_{\text{CH}}$				
C_2H_4		-0.999	-13.2	-2.4
C_2H_2		10.01	6.055	49.3

^a) taken from Ref [124]Table XIV. ^{13}C -H Couplings (Hertz) for Benzene and Napthalene.

System	Coupling	TDA	RPA	Experiment ^a
Benzene				
	$^1J_{11}$	157.6	214.7	159
	$^2J_{13}$	2.21	-3.30	1.1
	$^3J_{13}$	7.1	12.0	7.5
	$^4J_{14}$	-2.1	-11.0	-1.2
Napthalene				
	$^1J_{11}$	133.7	187.4	158
	$^2J_{12}$	0.769	-5.52	1.7
	$^3J_{13}$	8.43	13.7	8.6
	$^4J_{14}$	-0.112	-2.59	-1.5
	$^3J_{19}$	5.39	8.40	4.6
	$^2J_{21}$	1.22	-5.21	0.20
	$^1J_{22}$	151.3	207.9	159

Table XIV. (Continued) ^{13}C -H Couplings (Hertz) for Benzene and Napthalene.

$^2J_{23}$	0.841	-4.54	0.30
$^3J_{24}$	7.25	12.0	7.6

^{a)} taken from Ref [73]

In Table XIV, the various ^{13}C -H couplings for benzene and napthalene are given. The results are quite satisfactory. The RPA calculations predict anomalous signs in several situations. The FF calculations which have been reported for this system have the same sign error in each case⁷³.

Couplings Including the Dipolar and Orbital Terms

For the coupling between centers having valence-only functions with angular quantum number other than zero, the orbital and dipolar terms can contribute to J . The matrix elements for these operators are evaluated within the ZDO restriction as follows. For the orbital term, a typical non-zero matrix elements is determined from the raising/lowering quality of the magnetic dipole operator, and evaluated as an overlap integral

$$\langle 2p_{xN} | r_N^{-3} (\vec{r}_N \times \vec{\nabla}) | 2p_{yN} \rangle = -i \langle r^{-3} \rangle_N. \quad (5.45)$$

The value of $\langle r^{-3} \rangle_N$ is taken from the value obtained for the wavefunction of Herman-Skillman¹³⁸. Matrix elements of the dipolar operator are evaluated in a similar manner

$$\langle 2p_{xN} | r_N^{-5} (3r_{xN}^2 - r_N^2) | 2p_{xN} \rangle = \frac{4}{5} \langle r^{-3} \rangle_N. \quad (5.46)$$

Listed in Table XV are the ^{13}C couplings for some test cases, including contributions from all three perturbing Hamiltonians. The contact interaction dominates the calculated values in all cases. In general, the semiempirical results are much less impressive than the results of proton couplings. In several instances, the signs are opposite to experiment.

Table XV. The ^{13}C Couplings (Hertz) for Various Hydrocarbons.

System	Coupling	FC	OB	DP	Total	Experiment
	$^1J_{\text{CC}}$					
C_2H_2		147.5	8.05	5.10	160.6	171.5 ^a
C_2H_4		58.56	-8.15	2.32	52.73	67.6 ^a
Benzene						
	$^1J_{12}$	50.4	-5.69	0.85	45.5	57.0 ^b
Napthalene						
	$^1J_{12}$	40.82	-4.38	0.65	37.1	60.3 ^b
	$^2J_{24}$	-2.19	0.47	-0.27	-1.99	2.43
	$^4J_{29}$	4.14	0.43	0.28	4.85	5.45

^a) taken from Ref [124] ^b) taken from Ref [73]

The α -Coupling of ^{13}C and ^{19}F are presented in Table XVI. Although the signs are correctly predicted, the agreement with experiment is not particularly satisfying. It is interesting to note that the orbital contribution increases with increasing fluorine content, and that the dipolar term is more significant in the most polar molecules.

Table XVI The ^{13}C - ^{19}F Coupling (Hertz) in the Fluorinated Methane Series.

System	FC	OB	DP	Total	Experiment ^a
CH_3F	-211.4	2.22	16.9	-192.3	-157.5
CH_2F_2	-292.1	-17.1	3.0	-306.2	-234.8
CHF_3	-192.8	-29.2	6.9	-215.1	-274.3
CF_4	-150.9	-34.0	0.13	-184.8	-259.2

^a) taken from Ref [124]

CONCLUSION

Over the years, the main impetus for the development of semiempirical techniques of electronic structure theory was to compensate for the lack of computing power at hand. The explosive growth of the computer industry has drastically changed this situation. The advent of prolific high-speed, large-capacity computing environments has resulted in a stagnation in pure semiempirical research. This is mainly attributable to a sheer lack of manpower in this endeavor. The semiempirical approach is in fact experiencing competition from both extremes. The *ab initio* methods are ambitiously incorporating the latest advances in software, specifically designed to exploit the new generation of machines. This allows routine investigation on increasingly larger molecular systems at a sophisticated level of post-HF theory. From the other end of the spectrum, a new generation of entirely empirical molecular modelling packages are available. These programs contain huge data bases of bond distance, bond angle, and torsional angle parameters, and are proving to be invaluable in the pharmaceutical and biological sciences.

The cold war between theory and experiment has indeed reached a friendly *detente*. The practicing bench chemist no longer views quantum chemical techniques with disdain. More likely, the prudent experimentalist is apt to invest some time in a theoretical study to corroborate an intuition, or to give some clue as to where he or she should "look" in the molecular spectrum for the observable he hopes to detect. The experimental chemist who is shopping for a technique which suits his theoretical needs will likely settle for a method that performs at an attractive speed and cost, while still providing a reasonable degree of accuracy. For this reason alone, it is important that semiempirical methods are not abandoned.

The *ab initio* calculation employs the explicit evaluation of all components which enter into the SCF procedure. The selection of basis set expansion is crucial for the *ab initio* wavefunction, particularly depending on the specific property under investigation. Studies of basis set effects, along with the calculations of molecular wavefunctions which include various degrees of post-HF electron correlation are of utmost importance. These "experiments" give a benchmark to the minimal effort required for predictions which approach "chemical accuracy." They also test the quality of the underlying theory which is used to explain a particular phenomena. Highly accurate *ab initio* studies which disagree with laboratory results are now met with less skepticism from the experimental community, and in some instances have forced a re-thinking of experiment.

Much like the *ab initio* approach, the semiempirical philosophy is concerned with the evaluation of a molecular wavefunction towards the meaningful prediction of the properties of a system. To accomplish the HF SCF process, the semiempirical method employs an economical approach. Through the valence-only ZDO approximation and the use of experimental data, the semiempirical SCF can be performed extremely rapidly, while placing much less demand on computer storage. However, when a post-SCF procedure is undertaken, the semiempirical calculation loses its edge. When the atomic orbital representation is transformed to the molecular basis, the benefits of the ZDO restriction are lost, and transformations, diagonalizations, etc., become comparable in time and speed to a similar-sized *ab initio* calculation.

Towards the evaluation of properties in the framework of response functions, the algorithms which have been developed in this dissertation successfully circumvent the limitations which are imposed in the construction of states. The diagonalization-transformation steps which are inherent to the construction of CIS states are avoided through the inversion of the energy representation matrix. The inverse matrix is constructed from an iterative subspace of expansion vectors, and is accomplished by utilizing external stor-

age. In this manner, the process does not place an additional burden on RAM, and avoids excessive computer paging.

To streamline the inherent matrix multiplications of the inversion algorithm, the constituent two-electron integrals of the energy representation are processed in the atomic orbital basis. In effect, CIS properties are hence obtained directly from the atomic orbital basis. This form of integral processing dramatically improves the performance of the algorithm in two manners. First, the transformation of the integrals from the atomic to the molecular orbital basis is avoided. For the INDO procedure, this is at best an N^5 step, which is two orders of magnitude greater than the overall SCF process. Secondly, the integral lists in the atomic orbital basis benefit from the ZDO restrictions. When expanded to the molecular orbital basis the INDO integral list loses this advantage. The system time required to retrieve the integrals in the atomic basis is significantly less than that needed for the same operation in the molecular frame.

The direct, analytic evaluation of properties in this manner is actually more computationally efficient than finite field differentiation of the molecular energy. Considering the speed of the INDO SCF procedure, this is quite an accomplishment. Upon extension of the method to third-order, the benefits of the method are further enhanced. Because the result of the inverse product is essentially the expansion coefficients of the first-order wavefunction, these may be used, in accordance with the $2N+1$ rule of perturbation theory, to construct the third-order energy. The computational expense of obtaining the third-order energy is literally on the order of fractions of a CPU second, because it is basically a scalar product beyond the second-order value.

In its application to the frequency dependent polarizability, the algorithm need only be slightly modified to include the value of the frequency of interest in the diagonal elements of the matrix inversion procedure. By using the solution obtained at the previous frequency point as the starting guess for the subsequent point, the variance of the first

guess to the approximate inverse product is reduced by several orders of magnitude, and the convergence of the inversion is enhanced.

These features of the algorithm combine to integrate the sum-over-states procedure into the overall INDO philosophy. However, an efficient method of evaluating a property is of no consequence if the result of the effort is meaningless. An equally important aspect of this dissertation is the performance of the INDO procedure towards reproducing experimental and *ab initio* results. In addition, the question also arises as to what is the correct manner in which to systematically improve the semiempirical SCF wavefunction. Specifically, the INDO/S method is distinctly parameterized to reproduce electronic spectra from the CIS procedure. The INDO/S approach then naturally has a certain amount of correlation effects built into its parameterization scheme. Attempting to correct the INDO/S reference determinant through CI or many-body methods presents a "correlation-parameterization" dilemma. To maintain consistency, the ground state for an INDO/S calculation is best represented by the SCF single determinant, with excited states expanded as a linear combination of single-replacement determinants— via the CIS procedure. The results of this dissertation indeed verify that these choices are reasonable.

By enhancing the valence-only basis of the ZDO procedure with polarization functions on hydrogen atoms, the isotropic molecular polarizabilities predicted by the INDO/S TDA method are in good agreement with experiment. It is found that the polarization functions provide less of a percentage of the polarizability in larger molecules, which naturally have a valence-only basis which spans a larger area. However, the effect of polarization functions does not necessarily improve the anisotropy predicted by the INDO polarizability. The polarizability is found to be generally linear with the number of electrons in the system, with the TDA results invariably larger than the results of RPA calculations.

In the prediction of hyperpolarizability, the effect of basis set enhancement is found

to often have an opposite effect on the magnitude of the tensor components, by decreasing their value. This same trend is observed in the *ab initio* calculations, with almost constant regularity. With little exception, the hyperpolarizabilities predicted by the INDO/S TDA method are in much better agreement with *ab initio* results than the earlier study performed using CNDO/2 and the finite field technique.

The dynamic polarizability as predicted by the INDO/S procedure differs from that computed by large basis *ab initio* studies for the CO molecule, particularly in the direction perpendicular to the molecular axis. The discrepancy of the two methods is mainly attributable to the basis set deficiency of the valence-only method. This is further illustrated by calculations of the polarizability in the velocity and length formulations, and by calculations which include two center property integrals as well as those computed within the ZDO restriction. However, for the CH^+ ion, the INDO/S basis of five STO's has sufficient flexibility to mimic the *ab initio* calculation through several poles.

The INDO TDA predicted values of nuclear spin-spin coupling are very satisfactory for proton couplings and ^{13}C -H cases. For a minimal basis theory within the ZDO approximation the contact interaction is the only contributing phenomenon to the coupling. In several instances, the RPA method predicts an anomalous sign to the experimental coupling, and this phenomenon is also shared by the equivalent finite field calculations on the same systems. For couplings between ^{13}C nuclei, or between ^{13}C and ^{19}F , the orbital and dipolar contributions to the coupling must also be considered. These terms are in general underestimated because of the ZDO restriction, and the contact interaction continues to dominate the overall coupling constant. The resulting couplings are qualitative at best.

The opinion which should be drawn from this study is that INDO molecular properties can be calculated from the sum-over-states expression in an efficient manner, and can be relied upon, under the proper circumstances, to produce a result which carries some significance. The above statement contains a qualifier, for the INDO method

has especially proven successful when applied to certain classes of molecules, such as aromatics. Much like the situation of choosing a proper basis set expansion for a particular *ab initio* study, experience in semiempirical applications is necessary to ensure that the calculation in question is not asking too much of the model.

It is hoped that the methods of this dissertation will prove of some utility to the reader, or at least serve to ease some of the skepticism with which semiempirical work is greeted by *ab initio* proponents. For a concluding remark, The author would like to invite more theoreticians into the area of semiempirical research, because it is believed a great deal more could be accomplished in this field with more activity from the scientific community.

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BIOGRAPHICAL SKETCH

William Andrew Pakinson is a life-long underachiever. He attended high school in California, PA, where he met his future wife, Bonnie. The crowning achievement of his high school career was being named class clown for the senior yearbook. His undergraduate degree was obtained from California University in (no, not Berkeley) California, PA. This fact continues to provide a source of amusement to his colleagues. Upon graduation, he retired to St. Augustine, FL, where he worked variously as a high school teacher, a painter, a construction worker, a motel desk clerk, and a research chemist—but mostly he went to the beach and shot pool. With the birth of his first child, he decided to do something with himself, so he began attending UF as a graduate student in chemistry. For the first two years, he was actually foolish enough to commute all the way from Palatka, FL, a community some 60 miles from Gainesville. For some unknown reason, his wife Bonnie still puts up with him, and the family has expanded to include three children—Ryan, Daniel, and Casey. With the completion of his dissertation, he now hopes to get back into retirement soon.

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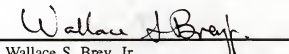
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Yngve Ohn,
Professor of Chemistry

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Wallace S. Brey, Jr.,
Professor of Chemistry

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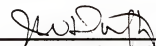
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Dean, Graduate School